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Kinetics of Homogeneous Reactions in Reaction Vessels with Ideal Mixing (Open Systems)

I.P.Skibida, Z.K.Maizus, and N.M.Emanuel'

The main kinetic features of chemical reactions occurring in flow systems with complete mixing are surveyed. The advantages are discussed of conducting a reaction in a flow system with stirring as compared with reactions under static conditions in a laminar flow. Considerable attention is paid to the establishment of oscillatory (pulsating) régimes. The dependence of the steady-state concentrations on the reaction conditions is examined, as also the kinetics of the establishment of a steady-state. A considerable part of the review is devoted to investigating the possibilities presented by open systems for studying the mechanism of chemical reactions and determining the rate constants of individual elementary stages in complicated chain processes. A list of 70 references is included.

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I. INTRODUCTION

Investigations of the kinetics of reactions in open systems, with continuous supply of the starting materials and withdrawal of the reaction products, arouse great interest in connection with the opportunities created for studying the mechanism of chemical reactions. These investigations are also of fundamental value because data on the mechanism and kinetics of reactions occurring in an open system are necessary for the design of present-day automatically controlled technical processes.

When a process is conducted under static conditions, certain quantities of starting materials are introduced into the system, and then undergo several chemical changes. In this case both the starting materials and the reaction products remain within the system: i.e. they do not leave

the reaction zone. The process is complete in a time determined by the quantity of starting materials taken and the rate constants of their conversion. The steady state, which is reached in some cases, represents the establishment of thermodynamic equilibrium. In an open system the unlimited supply and withdrawal of all the components of the reaction make it possible to establish a steady state differing from the thermodynamic equilibrium and characteristic not only for reversible but also for unidirectional reactions.

Processes with continuous supply and withdrawal of reactants can be conducted in two fundamentally different ways—under conditions of ideal (or complete) displacement and under conditions of ideal (complete) mixing†.

A vessel having ideal displacement is a reaction vessel into which a mixture of the reactants is introduced, and the reaction mixture is removed when a particular degree of conversion has occurred. Diffusion of the reactants in a vessel of ideal displacement should be reduced to a minimum. The composition of the reaction mixture in a given element of volume is determined solely by the extent of chemical reaction and varies along the length of the vessel. The residence time of all species in the reaction zone (the "contact time") is the same. Henceforward reactions occurring in vessels with ideal displacement will be termed "reactions in a flow".

The study of reactions in a flow is greatly complicated at high temperatures by convection currents and the presence of temperature gradients.

The second type of reaction vessel for conducting a reaction in a flow system is a "vessel with ideal mixing" (a "gradient-free reaction vessel"). In a vessel with ideal mixing the composition of the reaction products at a given time should be kept uniform throughout the volume by diffusion or by special mixing of freshly arriving substances with the partly reacted mixture. Such systems are also termed "open systems", since, in contrast to reactions in a streamlined flow, any given element of volume of the reaction mixture is "open" to freshly arriving substances. Change in the composition of the reaction mixture occurs not only as a consequence of chemical reaction but also as a result of the additional introduction of starting materials and reaction products from adjacent volumes. The residence times of species in the vessel are not the same. The mean residence time τ of species in the reaction volume is taken to be the reciprocal of the rate of supply of the starting materials to unit volume: i.e. $\tau = V/u$, where V is the volume of the reaction vessel and u the volume rate of supply of the reactants.

Both principles of an unenclosed system—reaction vessels of ideal displacement and of ideal mixing—are used in chemical technology. The latter are employed particularly in heterogeneous catalytic reactions and in other reactions involving solid particles, occurring in a "fluidised bed".

Several other chemical reactions can be more suitably conducted either in a laminar flow or with some definite degree of diffusion, which eliminates laminarity but does not guarantee complete mixing. However, it is fairly difficult to achieve conditions of complete laminarity and especially of a specified degree of diffusion, and in some cases, therefore, it is preferable to conduct the processes in several reaction vessels of ideal mixing connected in series.

† There may also be intermediate types of reaction vessels, with breakdown of laminar flow but not complete mixing.

To study reaction mechanisms it is also more convenient to use a "gradient-free reaction vessel", since the study of reactions in a streamlined flow requires either the careful elimination of or allowance for diffusion, the latter leading to rather unwieldy equations, which cannot be integrated in quadratures even for simple types of reactions.

The use of flow systems with complete mixing to investigate the kinetics of chemical reactions was initiated in 1905 by Bodenstein's work[1] on the kinetics of the reaction $H_2 + I_2 \rightleftharpoons 2HI$.

Conducting a reaction in a gradient-free reaction vessel enables the set of differential equations to be reduced to a set of algebraic equations, which considerably simplifies the task of determining the rate constants of complicated reactions.

Conducting a process in an open system has a further advantage over reactions under static conditions and in a laminar flow: it becomes possible to study processes over a considerably wider temperature range, since the continuous supply of starting materials to the system eliminates the possibility of the starting materials being completely burned up.

The present review will give an account of the main kinetic laws of homogeneous reactions occurring under conditions ensuring complete mixing with continuous supply and removal of substances to and from the reaction zone. We shall not discuss the kinetics of the series of heterogeneous processes in a flow examined in the works of Boreskov, Slin'ko, Temkin, Ioffe, Panchenkov, Nagiev, and other authors[2-6].

II. STEADY STATE IN AN OPEN SYSTEM

Various types of reaction vessel, with and without stirrers, can be used[7,8] to investigate homogeneous reactions in a flow with complete mixing, depending on the type of reaction and the necessary range of variation in flow rates.

For very rapid processes the completeness of mixing can be judged from the kinetics of the accumulation of reaction products being independent of the rate of mixing. With slower processes a method can be employed[9,10] in which a solution of a substance A, which undergoes no chemical change under the experimental conditions, is fed at a constant rate into a vessel filled with the pure solvent. The kinetics of the accumulation of this substance in the system will be described by the differential equation

$$\frac{d(a/a_0)}{dt} = \frac{u}{V} - \frac{u}{V}\left(\frac{a}{a_0}\right) \qquad (1)$$

where a_0 is the concentration of A in the solution fed into the vessel, u the volume flow rate, and V the volume of the system. Integration of Eqn. (1) yields

$$\ln\left(\frac{a_0}{a} - 1\right) = -\frac{u}{V} \cdot t \qquad (1a)$$

which describes the kinetics of the accumulation of A in the system. The slope of the semilogarithmic plot of $\ln[(a_0/a) - 1]$ against t will give the specific rate of supply of the starting materials to the system. Agreement between the experimental value of u/V and the value calculated from the known volume of the reaction vessel and the bulk rate of supply of A to the system indicates that mixing is complete in the vessel.

If a reaction occurring in an open system involves no change in volume, the concentrations both of the starting materials and of all intermediate and final products of the reaction will cease to change some time after the start of

the process: i.e. steady-state concentrations of all the components of the reaction are reached‡. A steady state can be defined as a state in which it is impossible to distinguish any macroscopic changes in the system[11]. Under these conditions the sum of the rates of formation of a product and of its supply to the reaction vessel is equal to the sum of its rates of consumption and removal from the reaction zone.

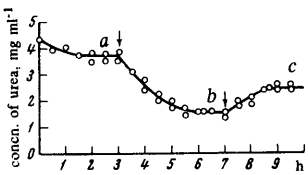


Figure 1. Steady-state concentrations of urea during its decomposition: a) in absence of an enzyme; b) in the presence of additions of an enzyme; c) on deactivation of the enzyme by $AgNO_3$ solution.

Establishment of a steady state in an open system has been observed with several simple and complicated reactions. Examples are the inversion of cane-sugar[9], the initiated polymerisation of styrene[12], the enzymic decomposition of urea[13] (Fig. 1), the decomposition of potassium persulphate catalysed by sulphuric acid[14], and the autoxidation of several hydrocarbons and their derivatives[15-17] (Fig. 2).

1. Time of Establishment of Steady State

If the concentration of a reaction product is zero at the start of a continuous process, the time of establishment of a steady state will depend solely on the rate of supply of the starting materials and the rate constants of the process[14]. The time for establishment of steady-state concentrations of the starting materials will differ from the corresponding time for the reaction products.

Let us examine the kinetics of the establishment of steady-state concentrations of starting material and reaction product in the case of a simple first-order reaction $A \xrightarrow{k_1} B$. The rate of consumption of the starting material A in the system is

$$\frac{da}{dt} = -\left(k_1 + \frac{u}{V}\right)a + \frac{u}{V}a_0.$$

Solution of this equation with the initial conditions $a = 0$ at $t = 0$ yields

$$-(k_1 + u/V)t = \ln\frac{(u/V)a_0 - (k_1 + u/V)a}{(u/V)a_0} = \ln\left(1 - \frac{a}{\bar{a}}\right) = \ln(1-\alpha) \quad (2)$$

where α is the degree of conversion and $\bar{a} = a_0 u/V[k_1 + (u/V)]$ is the steady-state concentration of A. It is seen that the time required to reach any given degree of conversion (e.g. $a = 0.99\bar{a}$, where $\bar{a}$ is the steady-state concentration) depends on the rate of flow and the rate constant k_1:

$$t_{99\%} = \frac{4.6}{k_1 + u/V}. \quad (3)$$

Conversion to 50% of the steady-state value is achieved at

$$t_{50\%} = \frac{0.639}{k_1 + u/V}. \quad (3a)$$

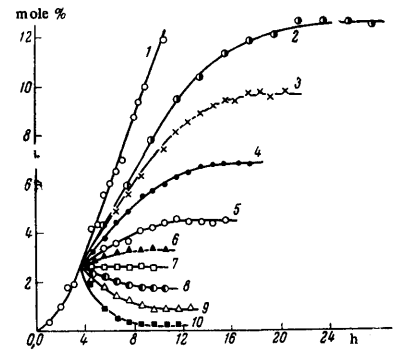


Figure 2. Kinetic curves for the accumulation of adipic acid by the oxidation of cyclohexanone in a reaction vessel of ideal mixing at 110°C with various rates of flow (h^{-1}): 1) 0; 2) 0.04; 3) 0.08; 4) 0.118; 5) 0.24; 6) 0.35; 7) 0.47; 8) 0.55; 9) 0.79; 10) 1.18.

We may note here that, when a first-order reaction is carried out in an open system, the time required to reach a definite degree of conversion of the starting material ($a = \alpha\bar{a}$) is independent of the concentration of A in the solution supplied to the vessel. This is analogous to the fact that under static conditions the time for a definite percentage conversion of the starting material to be achieved is independent of its initial concentration, being determined solely by the rate constant of the process.

The rate of accumulation of the final product B in a first-order reaction is given by the differential equation

$$\frac{db}{dt} = k_1 a - \frac{u}{V}b.$$

In this case

$$1 - \frac{b}{\bar{b}} = e^{-(u/V)\cdot t} - \frac{u}{Vk_1}e^{-(k_1+u/V)t}. \quad (4)$$

When a steady-state concentration of A ($a = 0.99\bar{a}$) is reached with $u/V = k_1$, we have $1 - (b/\bar{b}) = 0.09$: i.e. the steady-state concentration ($b = 0.99\bar{b}$) will not yet have been reached. Calculation based on Eqn. (4) with $u/V \simeq k_1$ shows that the time required for a steady-state concentration of the product B to be established will be approximately double the time required to reach a steady-state concentration of the starting material A.

For a reaction A + B → F with a rate constant of 0.002 M^{-1} min^{-1}, the time required for establishment of the steady-state concentration of a starting material has been shown to be 4τ, and that for the reaction product 6τ (calculations approximate to 1%).[12]

‡ If the system undergoes a change in volume, steady-state concentrations may not be achieved.

In the case of the polymerisation of styrene in the presence of benzoyl peroxide it has been found[12] that a steady-state concentration of styrene is reached in a time 7τ which is independent of the order of the reaction (the order may vary during the process and with different initial conditions). The calculations were based on the known rate constant for the consumption of styrene during polymerisation at 80°C.

2. Kinetics of Establishment of Steady State

The transition from one steady state to another with change in the conditions under which the process is occurring is of considerable interest. It is found that in several cases such transitions are not accomplished monotonically[8,13,14,18,19]: before the new steady state is reached the concentrations of the substances may pass through a maximum or a minimum. Two different phenomena are possible (see Fig. 3).

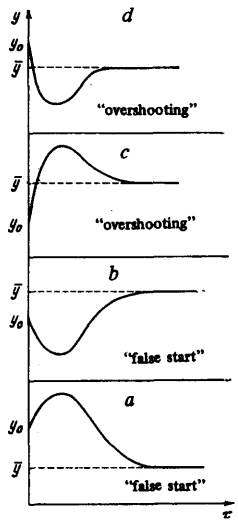


Figure 3. Diagrammatic representations of "overshooting" and "false start" phenomena when a reaction occurs in a vessel of ideal mixing.

1. In the phenomenon of the "false start" an initial change in some parameter of the system is immediately followed by a change in the concentration of the product in the opposite direction to that of the new steady-state concentration. Thus if the initial steady-state concentration of a substance A is a_0, and its new steady-state concentration a_1, a "false start" will give $(da/dt)_{t=t_0} < 0$ when $a_0 - a_1 < 0$ (a minimum is observed on the curve), or $(da/dt)_{t=t_0} > 0$ when $a_0 - a_1 > 0$ (a maximum is observed on the curve).

2. In the "overshooting" phenomenon the initial change in the concentration of a substance is towards the new steady-state concentration: with $a_0 - a_1 < 0$ we have $(da/dt)_{t=t_0} > 0$, and with $a_0 - a_1 > 0$ the derivative $(da/dt)_{t=t_0} < 0$. At a certain time the concentration of the reaction product exceeds the steady-state value (or is lower than the latter), and only by passing through a maximum (or minimum) is the steady-state value reached.

The conditions under which a "false start" or "overshooting" occurs have been determined for a first-order reversible reaction $A \rightleftharpoons B$ and the consecutive reaction $A \rightarrow B \rightarrow C$ when the rates of supply of starting material and of removal of reaction products differ greatly[14] and also when they are the same[8].

Let us examine in rather greater detail the possibility of the occurrence of a "false start" and "overshooting" on the kinetic curves for the accumulation of reaction products in the consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ with identical rates of supply and removal of all products[8]. In this case, denoting the concentrations of A and B by x and y, we can write down the set of differential equations

$$\frac{dx}{dt} = -(k_1 + u/V)\,x + \frac{u}{V}\tilde{x}_0 \qquad (5)$$

where $\tilde{x}_0$ is the concentration of the component A in the solution fed to the vessel, and

$$\frac{dy}{dt} = k_1 x - (k_2 + u/V)\,y\,. \qquad (6)$$

Introducing the new variables $\Delta x = x - \bar{x}$ and $\Delta y = y - \bar{y}$ (where $\bar{x}$ and $\bar{y}$ are the steady-state concentrations of A and B respectively), and remembering that

$$\frac{d\bar{x}}{dt} = -(k_1 + u/V)\,\bar{x} + \frac{u}{V}\tilde{x}_0 = 0 \qquad \frac{d\bar{y}}{dt} = k_1\bar{x}_0 - (k_2 + u/V)\,\bar{y} = 0$$

we can reduce the differential equations (5) and (6) to the form

$$\frac{d\Delta x}{dt} = -(k_1 + u/V)\,\Delta x \qquad (7)$$

$$\frac{d\Delta y}{dt} = k_1\Delta x - (k_2 + u/V)\,\Delta y. \qquad (8)$$

Integration of (7) and (8) will give

$$\Delta x = \Delta x_0 e^{-(k_1+u/V)(t-t_0)}$$

$$\Delta y = \frac{k_1\Delta x_0}{k_2-k_1}\{e^{-(k_1+u/V)(t-t_0)} - e^{-(k_2+u/V)(t-t_0)}\} + \Delta y_0 e^{-(k_2+u/V)(t-t_0)}$$

where $\Delta x_0 = x_0 - \bar{x}$ and $\Delta y_0 = y_0 - \bar{y}$ are the deviations in the concentrations x and y in the system from the steady-state values at $t = t_0$ (where t_0 corresponds to the instant of transition from the continuous régime, change in the rate of flow, etc.).

The derivative

$$\frac{d\Delta y}{dt} = (k_2 + u/V)\left[\frac{k_1\Delta x_0}{k_2-k_1} - \Delta y_0\right] e^{-(k_2+u/V)(t-t_0)} - \frac{k_1\Delta x_0}{k_2-k_1} e^{-(k_1+u/V)(t-t_0)}$$

can vanish as $t \to \infty$, which corresponds to the establishment of a steady state, and also when

$$(t-t_0) = \frac{1}{k_2-k_1}\ln\left\{\left[1 - \frac{\Delta y_0\,(k_2-k_1)}{k_1\Delta x_0}\right]\frac{k_1+u/V}{k_1+u/V}\right\}. \qquad (9)$$

If Eqn. (9) is satisfied, extremal values appear on the kinetic curves for accumulation of the intermediate substance.

Analysis of Eqn. (9) together with the differential equation (8) will give the following conditions for the appearance of "overshooting" and a "false start" on the kinetic curve for the accumulation of the intermediate B in the above consecutive reaction[8].

1. If $\Delta x_0 > 0$ and $\Delta y_0 > 0$ at zero time, a "false start" with a maximum on the curve may be observed at values of $u/V < (k_1\Delta x_0/\Delta y_0) - k_2$.

2. With $\Delta x_0 < 0$ and $\Delta y_0 < 0$ a "false start" with a minimum may be observed at velocities

$$u/V < \frac{k_1 \Delta x_0}{\Delta y_0} - k_2 .$$

3. When $\Delta x_0 > 0$ and $\Delta y_0 < 0$ "overshooting" with a maximum can be observed throughout the range of variation in u/V, and when $\Delta x_0 < 0$ and $\Delta y_0 > 0$ "overshooting" with a minimum on the kinetic curve can occur.

The phenomena of a "false start" and "overshooting" have been observed experimentally in particular on the kinetic curve for the accumulation of sulphuric acid (the final product of the decomposition of potassium persulphate (Fig. 4*a*) accompanied by the liberation of atomic oxygen[14])

$$K_2S_2O_8 + H_2O \rightarrow K_2SO_4 + H_2SO_4 + O$$

and also in the enzymic decomposition of urea in the presence of urease and additions of silver nitrate, causing inactivation of the enzyme[13], as well as in the complicated chain oxidations of n-decane and ethylbenzene by atmospheric oxygen (Fig. 4*b*).[8]

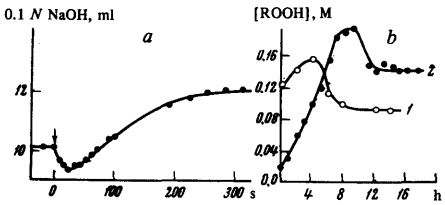


Figure 4. (a) "False start" on kinetic curve for accumulation of sulphuric acid during decomposition of aqueous potassium persulphate solution in reaction vessel of ideal mixing. The arrow indicates the instant at which the rate of diffusion changes. (b) Kinetic curves for accumulation of hydroperoxides in the oxidation of n-decane in a reaction vessel of ideal mixing at 140°C: 1) "false start"; 2) "overshooting".

The possibility of the appearance of "overshooting" and "false starts" on kinetic curves for the consumption of starting material in an open system has been examined in a previous paper[20]. If the reaction is of the first order (see above) the derivative

$$-\frac{d\Delta x}{dt} = \Delta x_0 (k_1 + u/V) e^{-(k_1 + u/V)/(t - t_0)}$$

is able to vanish only at $t = t_\infty$, i.e. in a steady state. At all values of $t \neq t_\infty$ the concentration of the starting material either increases monotonically when $\Delta x_0 < 0$ or falls monotonically when $\Delta x_0 > 0$. Consequently the concentration of the initial reactant can only vary monotonically on passing from one stationary state to another: the occurrence of any extrema is then impossible. This holds for a non-autocatalytic reaction of any order[20].

In fact, for a reaction of the nth order we have

$$\frac{d[A]}{dt} = -k_1[A]^n - (u/V)[A] + (u/V)[A]_0$$

and when $d[A]/dt = 0$ the second derivative

$$\frac{d^2[A]}{dt^2} = [-k_1 n [A]^{n-1} - u/V] \frac{d[A]}{dt} \equiv 0$$

which corresponds to the establishment of a steady state. Thus the kinetic curve for the consumption of A cannot pass through extrema.

In autocatalytic reactions, unlike those of simple types, "overshooting" and "false start" phenomena can be observed even on the kinetic curves for the consumption of the starting material[20]. Actually, if the starting material A is consumed autocatalytically by interacting with the reaction product B, its rate of accumulation in the system is described by the differential equation

$$\frac{d[A]}{dt} = -k_1[A][B] - \frac{u}{V}[A] + \frac{u}{V}[A]_0 .$$

At the instant at which $d[A]/dt = 0$ the second derivative

$$\frac{d^2[A]}{dt^2} = -k_1[A]\frac{d[B]}{dt} - \left[k_1[B] + \frac{u}{V}\right]\frac{d[A]}{dt}$$

may differ from zero if at this instant $d[B]/dt \neq 0$. In this case the kinetic curve for consumption of A will pass through a maximum or a minimum before a steady state is attained.

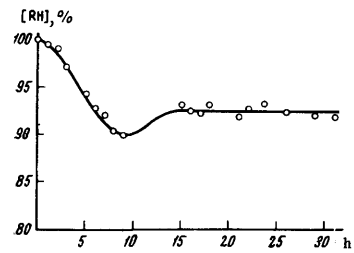


Figure 5. "Overshooting" on kinetic curve for consumption of ethylbenzene by oxidation in an open system at 118°C with a rate of flow of 0.102 h^{-1}.

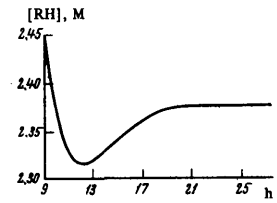


Figure 6. Kinetic curve for consumption of starting material in catalysed oxidation, calculated on M-20 electronic computer with [RH] = 5.2 M, [$CoSt_2$] = 0.006 M, and $u/V = 5 \times 10^{-5}$ s^{-1}.

The phenomenon of "overshooting" has been observed, for example, on the kinetic curve for the consumption of ethylbenzene during its autoxidation by oxygen (Fig. 5).[10]

The possibility of the appearance of extrema on kinetic curves for the consumption of the starting material has been shown also in the catalysed oxidation of hydrocarbons

in the presence of cobalt stearate[21]. The mechanism of the process in this case is represented by the scheme

$$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot} \quad (k_1)$$

$$ROOH + CoSt_2 \rightleftarrows ROOH \cdot CoSt_2 \quad (k_2,\ k_3)$$

$$ROOH \cdot CoSt_2 + CoSt_2 \rightarrow RO^{\cdot} + Co(OH)St_2 + CoSt_2 \quad (k_4)$$

$$ROOH + Co(OH)St_2 \rightarrow CoSt_2 + H_2O + RO_2^{\cdot} \quad (k_5)$$

In an open system the oscillations are maintained indefinitely. When malonic acid was replaced by malic acid, for example, oscillation at two frequencies was observed[29] under certain conditions (Fig. 8).

The very fact that periodic chemical reactions can occur is very interesting from the points of view both of chemical kinetics and of biology. Among the clearest periodic processes in biology are the biological systems for recording

The dependence of the steady-state concentration of radicals $\bar{n}$ on the initial concentration of inhibitor i_0 is found by solving the cubic equation

$$\bar{n}^3 - \frac{1}{k_6}\left(\frac{2k_2k_3[RH]}{(k_3 + u/V)} - \frac{u}{V} - \frac{uk_5}{Vk_i}\right)\bar{n}^2 + \\ + \frac{u}{Vk_6k_i}\left(k_i \cdot i_0 - \frac{2k_2k_3[RH]}{(k_3 + u/V)} + \frac{u}{V} - \frac{w_0k_i \cdot V}{u}\right)\bar{n} - \frac{u \cdot w_0}{Vk_ik_6} = 0 . \quad (11)$$

Equation (11) has three positive roots $\bar{n}_1$, $\bar{n}_2$, $\bar{n}_3$ (three steady states of the process) provided that

$$\frac{V}{u}\left[\frac{2k_2k_3[RH]}{(k_3 + u/V)} - \frac{u}{V}\right] > \frac{k_5}{k_i} .$$

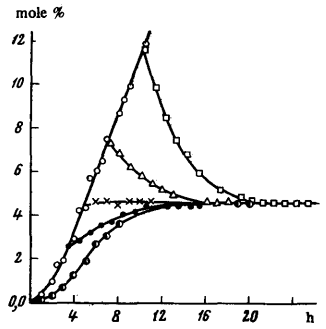


Figure 9. Kinetic curves for the accumulation of adipic acid during the continuous oxidation of cyclohexanone at 110°C with a rate of flow of 0.265 h^{-1}.

However, analysis shows that one of the solutions is unstable. The dependence of the steady-state concentration of the primary intermediate product, the hydroperoxide ROOH (the concentration of hydroperoxide is proportional to the concentration of radicals n), on the initial concentration of the inhibitor[42] is shown graphically[44] in Fig. 10. The section afb corresponds to the steady state $\bar{n}_1$, and the section cd determines $\bar{n}_3$. The state $\bar{n}_2$ (branch blc) is unsteady and is not realised.

Experimental data on the dependence of the steady-state concentration of a reaction product on the initial conditions have been obtained in an investigation of the inhibited oxidation of n-decane[42]. The steady-state hydroperoxide concentration is found to depend on the initial concentration

with change in the inhibitor concentration right until the latter corresponds to point b. At this inhibitor concentration the steady state of the system changes in the direction indicated by the arrow. Thus it is seen that, with the same inhibitor concentration in the solution fed to the vessel and different initial hydroperoxide concentrations in the system ($[ROOH]_0$ = 1.2 mole % and 0), two markedly different steady states are attained. The broken section b–c defines the magnitude of the unstable steady state. In the oxidation of n-decane containing hydroperoxide from the start, breaks are observed close to the critical inhibitor concentration on the kinetic curve of the hydroperoxide (sections a–b on the curves in Fig. 12).[42]

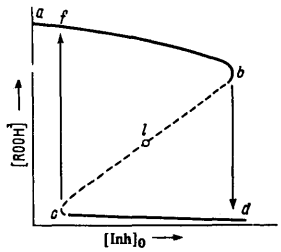


Figure 10. Dependence of steady-state concentration of hydroperoxide on initial concentration of inhibitor in a continuous process of oxidation (calculated results).

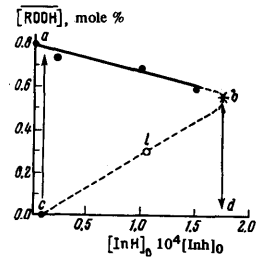


Figure 11. Dependence of steady-state concentration of hydroperoxide on concentration of 1-naphthol and initial hydroperoxide concentration in the system during the oxidation of n-decane with continuous supply of a solution of 1-naphthol in n-decane, at 135°C with rate of flow 1.45×10^{-4} s^{-1}.

With certain initial conditions[34] auto-oscillations can be expected also in a first-order exothermic reaction A → B under non-isothermal conditions.

Auto-oscillations can occur when the process can be described by a set of non-linear differential equations.

The possibility of the occurrence of oscillations has since been discussed theoretically for a large number of systems. In particular, detailed analysis has shown[35-37] that oscillations are impossible under isothermal conditions in systems in which only simple types of reactions take place. Only the presence of an autocatalytic stage or of a wall reaction can lead to the appearance of oscillations[37].

In the system

$$A_1 + M_1 \rightarrow M_2 + B_1$$
$$A_2 + M_2 \rightarrow M_3 + B_2$$
$$A_3 + M_3 \rightarrow M_1 + B_3$$

where the M_i are catalysts, damped and undamped oscillations are possible if the number of components in the reaction exceeds 3.

The occurrence of oscillations about a steady-state value has been discussed in detail for a consecutive reaction comprising n stages, all of which are autocatalytic, taking place in an open system[38]. It is shown that harmonic oscillations about a steady-state value should be observed if the number of consecutive stages does not exceed 3. If the number of stages does exceed 3, anharmonic oscillations are produced owing to the superposition of oscillations. The occurrence of oscillations, and also their frequency and amplitude, depend on the rate of supply of the starting materials to the system and on the initial conditions.

A detailed discussion of oscillatory phenomena in chemical and biological systems will be found in Ref. 39.

IV. DEPENDENCE OF STEADY-STATE CONCENTRATION ON CONDITIONS OF PROCESS

The steady-state concentration is determined by the parameters of the system (temperature, pressure, presence of a catalyst or an inhibitor, and also the rate of flow).

The change in the steady state produced by addition of a catalyst to a system has been shown, for example, in the enzymic decomposition of urea[13] and the decomposition of aqueous potassium persulphate solutions catalysed by silver sulphate[14]. It was shown in the former case[13] that different steady-state concentrations of urea are established in the system depending on the degree of inactivation of the enzyme by silver nitrate solution (Fig. 1). In the decomposition of potassium persulphate in aqueous solutions a change in the steady-state concentration of sulphuric acid (a reaction product) has also been observed on the addition of a catalyst (silver sulphate) to the system[14].

It is interesting that, if a reversible reaction is taking place in an open system, addition of a catalyst not only increases the rate of establishment of equilibrium, as occurs in a closed system, but also leads to a shift in the thermodynamic equilibrium[13a]. This phenomenon has been investigated theoretically[13a] for the first-order reversible reaction A ⇌ B.

Variation in temperature also influences the steady-state concentrations in a system. For example, the mean degree of vinyl polymerisation falls with rise in temperature[40] (this parameter is a function of the concentration of the monomer).

1. Dependence of Steady-State Concentration on Initial Conditions

For most reactions, having highly diverse mechanisms, the steady-state concentration under gradient-free conditions is independent of the concentration of products in the system at the instant of transition to a continuous régime. In the simplest case, when a substance A is consumed by a first-order reaction having a rate constant k_1, we have for the rate of the process the equation

$$\frac{da}{dt} = -(k_1 + u/V)a + (u/V)a_0 . \qquad (10)$$

Integration gives

$$-(k_1 + u/V)a + (u/V)a_0 = [(u/V)a_0 - (k_1 + u/V)a_1]e^{(k_1+u/V)t}$$

where a_1 is the concentration of A in the vessel at time $t = 0$. As $t \rightarrow \infty$ a concentration $\bar{a}$ is reached, which remains unchanged with time (steady-state concentration), and is given by

$$\bar{a} = \frac{(u/V)a_0}{(k_1+u/V)} .$$

This is independent of a_1, and is determined by the values of k_1 and u/V.

The same formula for $\bar{a}$ can be obtained by equating the derivative da/dt in Eqn. (10) to zero.

More generally we can write for the accumulation in an open system of a substance X, formed at a rate w_f and consumed at a rate w_u, the equation

$$\frac{dx}{dt} = w_f - w_u + (u/V)x_f - (u/V)x .$$

In this case the steady-state concentration $\bar{x}$ (determined from the condition $dx/dt = 0$) is given by

$$\bar{x} = \frac{w_f - w_u}{u/V} + x_0$$

being dependent only on x_0, the rates of formation and consumption of X, and the rate of flow, but not on the concentration of X in the vessel at the start of the continuous process.

The fact that the steady-state concentration is independent of the initial conditions can be illustrated, for example, by the series of kinetic curves for the accumulation of adipic acid in the autoxidation of cyclohexanone, obtained with different initial degrees of oxidation (Fig. 9).[15]

Autocatalytic reactions in which two stable steady states can occur depending on the initial conditions constitute an exception. This case has been analysed in the literature[14,34,41-43].

The possibility of more than one steady state appearing in such a system has been investigated in detail by Andreev[41] on the basis of an actual scheme for the oxidation of hydrocarbons in the presence of inhibitors which terminate the oxidation chains

$$RH \rightarrow RO_2^{\bullet} \qquad (w_0)$$
$$RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \qquad (k_2)$$
$$ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH \qquad (k_3)$$
$$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow \text{chain termination} \qquad (k_4)$$
$$RO_2^{\bullet} + \text{Inh} \rightarrow \text{chain termination} \qquad (k_i) .$$

The dependence of the steady-state concentration of radicals $\bar{n}$ on the initial concentration of inhibitor i_0 is found by solving the cubic equation

$$\bar{n}^3 - \frac{1}{k_5}\left(\frac{2k_2k_3[RH]}{(k_3+u/V)} - \frac{u}{V} - \frac{uk_5}{Vk_t}\right)\bar{n}^2 + \\ + \frac{u}{Vk_5k_t}\left(k_t \cdot i_0 - \frac{2k_2k_3[RH]}{(k_3+u/V)} + \frac{u}{V} - \frac{w_0k_t \cdot V}{u}\right)\bar{n} - \frac{u \cdot w_0}{Vk_tk_5} = 0 . \quad (11)$$

Equation (11) has three positive roots $\bar{n}_1$, $\bar{n}_2$, $\bar{n}_3$ (three steady states of the process) provided that

$$\frac{V}{u}\left[\frac{2k_2k_3[RH]}{(k_3+u/V)} - \frac{u}{V}\right] > \frac{k_5}{k_t}.$$

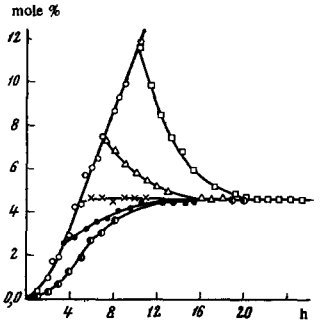


Figure 9. Kinetic curves for the accumulation of adipic acid during the continuous oxidation of cyclohexanone at 110°C with a rate of flow of 0.265 h^{-1}.

However, analysis shows that one of the solutions is unstable. The dependence of the steady-state concentration of the primary intermediate product, the hydroperoxide ROOH (the concentration of hydroperoxide is proportional to the concentration of radicals n), on the initial concentration of the inhibitor[42] is shown graphically[44] in Fig. 10. The section afb corresponds to the steady state $\bar{n}_1$, and the section cd determines $\bar{n}_3$. The state $\bar{n}_2$ (branch blc) is unsteady and is not realised.

Experimental data on the dependence of the steady-state concentration of a reaction product on the initial conditions have been obtained in an investigation of the inhibited oxidation of n-decane[42]. The steady-state hydroperoxide concentration is found to depend on the initial concentration of hydroperoxide in the system. Fig. 11 illustrates experimental results on the inhibited oxidation of pure n-decane and of n-decane containing 1.2 mole % of the hydroperoxide before the start of the reaction. The point a on this diagram indicates the steady-state hydroperoxide concentration in the absence of inhibitor, this being 0.8 mole % under the experimental conditions. If the pure hydrocarbon is being oxidised, the steady state of the system at high inhibitor concentrations is represented by the section c–d. At an inhibitor concentration corresponding to point c a sharp change occurs in the steady state of the system, in the direction indicated by the arrow. If the hydrocarbon contains a certain quantity of the hydroperoxide $[ROOH]_0 > a$ at the start of the reaction, the concentration of hydroperoxide in the steady state will vary along the section a–b with change in the inhibitor concentration right until the latter corresponds to point b. At this inhibitor concentration the steady state of the system changes in the direction indicated by the arrow. Thus it is seen that, with the same inhibitor concentration in the solution fed to the vessel and different initial hydroperoxide concentrations in the system ($[ROOH]_0$ = 1.2 mole % and 0), two markedly different steady states are attained. The broken section b–c defines the magnitude of the unstable steady state. In the oxidation of n-decane containing hydroperoxide from the start, breaks are observed close to the critical inhibitor concentration on the kinetic curve of the hydroperoxide (sections a–b on the curves in Fig. 12).[42]

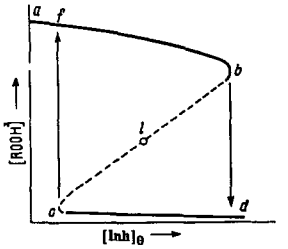


Figure 10. Dependence of steady-state concentration of hydroperoxide on initial concentration of inhibitor in a continuous process of oxidation (calculated results).

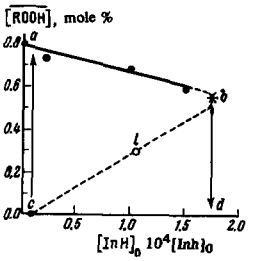


Figure 11. Dependence of steady-state concentration of hydroperoxide on concentration of 1-naphthol and initial hydroperoxide concentration in the system during the oxidation of n-decane with continuous supply of a solution of 1-naphthol in n-decane, at 135°C with rate of flow 1.45×10^{-4} s^{-1}.

With exothermic processes different steady states can be established according to the initial conditions even for simple types of reactions. The occurrence of two greatly differing régimes when a reaction is conducted under adiabatic conditions in a gradient-free reaction vessel was first established by Zel'dovich[43] for thermal ignition. It has been shown[34] that different steady states may be established, depending on the initial conditions, when a first-order exothermic reaction is conducted under non-isothermal conditions in a gradient-free vessel.

Thermal ignition phenomena with a sharp transition from a steady state to a non-stationary régime are inherent in exothermic processes even under static conditions. However, open systems are distinguished by sharper boundaries between ignition and a steady state. When exothermic processes are conducted in open systems, the possibility arises of determining the true concentration limit of ignition (this is impossible under static conditions because the mixture is consumed).

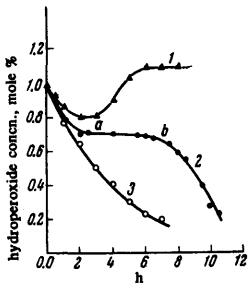


Figure 12. Kinetic curves for the accumulation of hydroperoxide in the oxidation of n-decane containing an initial hydroperoxide concentration of 1.0 mole % at 135°C with a rate of flow of 1.45×10^{-4} s^{-1}, and with different inhibitor concentrations (M) in the solution fed into the vessel: 1) 4.0×10^{-4}; 2) 4.1×10^{-4}; 3) 4.3×10^{-4}.

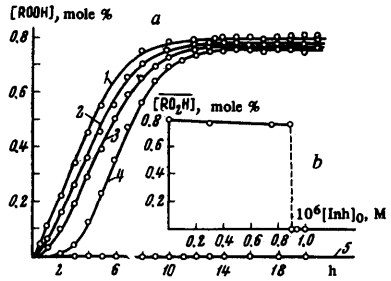


Figure 13. (a) Kinetic curves for the accumulation of hydroperoxide in the continuous oxidation of n-decane at 120°C, with rate of flow of 0.53 h^{-1}, in the presence of 1-naphthol (M): 1) 0; 2) 3×10^{-6}; 3) 7.5×10^{-6}; 4) 9.0×10^{-6}; 5) 9.05×10^{-6}. (b) Dependence of steady-state concentration of hydroperoxide on initial concentration of 1-naphthol.

A greater sharpness of critical transitions in open than in static systems has been observed also in an investigation of the inhibited oxidation of n-decane[45]. The inhibitors used were 1-naphthol and tri-(3,5-di-t-butyl-4-hydroxybenzyl)amine, under identical temperature conditions in open and static systems. When the process is conducted continuously a very sharp transition is observed from the autocatalytic reaction to the steady-state reaction at a critical inhibitor concentration[45] (Fig. 13). Under the same conditions in a closed system the induction period of the process increases linearly with increase in the inhibitor concentration, and limiting phenomena are not observed[42] (Fig. 14). The causes of the sharpness in the transitions in open systems have been analysed[42].

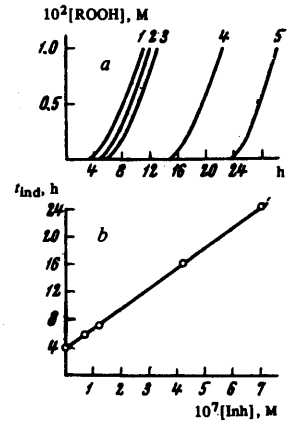


Figure 14. (a) Kinetic curves for the accumulation of hydroperoxide in the oxidation of n-decane under static conditions at 120°C with different initial concentrations (M) of inhibitor (1-naphthol): 1) 0; 2) 8×10^{-7}; 3) 1.2×10^{-6}; 4) 4.1×10^{-6}; 5) 7×10^{-6}. (b) Dependence of induction period on inhibitor concentration.

2. Dependence of Steady-state Concentration on Flow Rate

The variation in steady-state concentrations with change in the rate of supply of the starting materials has been discussed in the greatest detail in the literature. It has been shown for simple reactions (of the first, second, and third order) that increase in the rate of supply of starting materials (and of withdrawal of reaction products) diminishes the steady-state concentration of reaction products, while that of the starting materials increases monotonically[46].

As example let us examine the reaction $A \xrightarrow{k_1} C$, where conversion of A into the product is a first-order reaction. Then the variation in the concentrations of A and C will be described by the differential equations

$$\frac{d[A]}{dt} = -k_1[A] - \frac{u}{V}[A] + \frac{u}{V}[A]_0$$

$$\frac{d[C]}{dt} = k_1[A] - \frac{u}{V}[C],$$

where u is the bulk rate of supply of the substances, V is the volume of the system, $[A]_0$ is the concentration of A in the solution entering the vessel, and [A] and [C] are the instantaneous concentrations of A and C in the solution.

In the steady state $d[A]/dt = d[C]/dt = 0$, and the steady-state concentrations are

$$[\bar{A}] = \frac{(u/V)[A]_0}{(k_1 + u/V)} \qquad (12)$$

$$[\bar{C}] = \frac{k_1[\bar{A}]}{u/V} = \frac{k_1[A]_0}{(k_1 + u/V)} \qquad (13)$$

With increase in u/V the steady-state concentration of C will fall, while that of A will increase, since the factor $u/V(k_1 + u/V)$ increases with increase in u/V.

Analogous equations can be written for second- and third-order reactions[9,46].

The steady-state concentration of the intermediate product in a consecutive reaction will depend in more complicated fashion on the flow rate.

With increase in the rate of supply of the starting materials the steady-state concentration of the intermediate in the consecutive reaction A → B → C first increases and then falls. This extremal dependence on u/V is due to the fact that increasing this parameter produces an increase in the steady-state concentration of the initial substance A, which results in an increase in the concentration of B, while the more rapid removal of B from the system tends to diminish its steady-state concentration.

This can be illustrated by the interaction of the iron(III) ion with the thiosulphate ion[47]

$$2Fe^{3+} + 2S_2O_3^{2-} \rightarrow 2Fe^{2+} + S_4O_6^{2-}.$$

The reaction involves intermediate formation of an unstable complex between these two ions. Determination of the concentration of this complex has shown that its steady-state concentration passes through a maximum with increase in the rate of flow (Fig. 15).

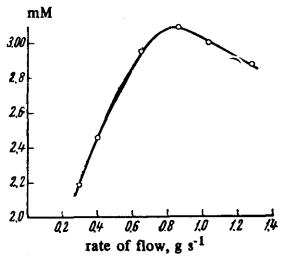


Figure 15. Dependence of steady-state concentration of intermediate complex in the reaction of Fe^{3+} with the thiosulphate ion on rate of supply of $S_2O_3^{2-}$ (rate of supply of Fe^{3+} constant at 0.388 g s^{-1}).

The rate of flow at which the maximum steady-state concentration of the intermediate is reached will depend on the rate constants of its formation and consumption[48]. In the simple consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, for example, the variation in the concentration of the intermediate substance B is given by the differential equation

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] - \frac{u}{V}[B].$$

The steady-state concentration of B is

$$[\bar{B}] = \frac{k_1 \frac{u}{V}[A]_0}{(k_1 + u/V)(k_2 + u/V)}. \qquad (14)$$

It is seen from Eqn. (14) that the steady-state concentration $[\bar{B}] \rightarrow 0$ as $u/V \rightarrow 0$ and as $u/V \rightarrow \infty$. Since $[\bar{B}]$ has some value different from zero within the range of variation of u/V from 0 to ∞, the steady-state concentration of B must pass through a maximum with increase in u/V. Differentiating $[\bar{B}]$ with respect to u/V, we obtain

$$\frac{d[\bar{B}]}{d(u/V)} = \frac{[A]_0 k_1 [k_1 k_2 - (u/V)^2]}{(k_1 + u/V)^2 (k_2 + u/V)^2}.$$

The dependence of $[\bar{B}]$ on u/V will pass through a maximum when $d[\bar{B}]/d(u/V) = 0$, i.e. at a rate of flow $u/V = \sqrt{k_1 k_2}$.

If more than one intermediate is formed in the system, the steady-state concentration of each product should pass through a maximum, and that of the first intermediate should be reached at higher rates of flow than that of the second intermediate[8]. Thus in the consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$ the maximum steady-state concentration of B is reached at a rate of flow u/V satisfying the condition $d[\bar{B}]/d(u/V) = 0$. For the steady-state concentration of the second intermediate C we have

$$\frac{d[C]}{dt} = k_2[B] - k_3[C] - u/V[C]; \quad [\bar{C}] = \frac{k_1[\bar{B}]}{k_3 + u/V}.$$

At the maximum in $[\bar{B}]$, when $d[\bar{B}]/d(u/V) = 0$, we find that

$$\frac{d[\bar{C}]}{d(u/V)} = -\frac{k_1[\bar{B}]}{(k_3 + u/V)^2} + \frac{k_1}{(k_3 + u/V)} \cdot \frac{d[\bar{B}]}{d(u/V)} < 0,$$

i.e. $[\bar{C}]$ is a diminishing function of u/V. This implies that the maximum value of C is reached at lower values of u/V than is $[\bar{B}]_{max}$.

The above rules for the variation in steady-state concentrations of final and intermediate products and of starting materials with rate of flow, derived for simple reactions, are maintained for more complicated processes.

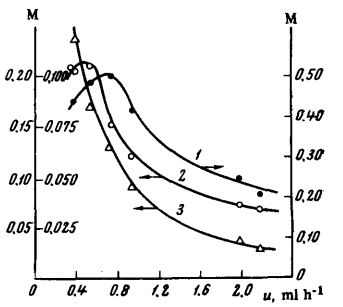


Figure 16. Dependence of steady-state concentrations of oxidation products on rate of supply of ethylbenzene at 118°C: 1) hydroperoxide (right-hand scale); 2) 1-phenylethanol (outer left-hand scale); 3) acetophenone (inner left-hand scale).

An example is the liquid-phase oxidation of ethylbenzene in the presence of azoisobutyronitrile as initiator[17]. The process goes by a chain mechanism with the following sequence of products

ethylbenzene → α-hydroperoxide → 1-phenylethanol → acetophenone

Thus two intermediate products—the hydroperoxide and the carbinol—and one final product—acetophenone—are formed in the system. Investigation of the oxidation of ethylbenzene in a gradient-free reaction vessel has shown that with increase in the flow rate the steady-state concentrations both of the hydroperoxide and of the carbinol pass through a maximum (Fig. 16). In complete agreement with what

has been stated above, the maximum steady-state concentration of the alcohol is reached at lower rates of flow than is that of the hydroperoxide. The steady-state concentration of the ketone falls monotonically with increase in u/V (Fig. 16).

Systems can also exist in which the above variation in steady-state concentration with rate of flow does not occur. Among them are processes involving the intermediate formation of complexes, e.g. by the scheme

$$\begin{aligned} A &\rightarrow B \quad (k_1) \\ B + C &\rightleftarrows D \quad (k_2, k_{-2}) \\ D &\rightarrow E \quad (k_3) \ . \end{aligned}$$

If equilibrium is established sufficiently rapidly and is not disturbed, either by conversion of D into E or by withdrawal of D from the system, i.e. provided that

$$k_3[D] \ll k_{-2}[D] \gg \frac{u}{V}[D]$$

the steady-state concentration of B will not pass through a maximum[49]. The steady-state concentration of A in such a system is

$$[\bar{A}] = \frac{(u/V)[A]_0}{(k_1 + u/V)}$$

while the rate of change in the concentration of B is described by the differential equation

$$\frac{d[B]}{dt} = k_1[A] - k_2[B][C] + k_{-2}[D] - \frac{u}{V}[B].$$

When thermodynamic equilibrium is maintained $k_2[B][C] = k_{-2}[D]$ and $d[B]/dt = k_1[A] - (u/V)[B]$. The steady-state concentration of the intermediate B

$$[\bar{B}] = \frac{k_1 V}{u}[A] = \frac{k_1[A]_0}{k_1 + u/V}$$

increases steadily with decrease in u/V, tending to $[A]_0$, and does not pass through a maximum.

The absence of a maximum steady-state concentration of an intermediate product has been shown for the oxidation of n-decane catalysed by cobalt stearate[21,49]. As already mentioned above (Section II, 2), breakdown of the hydroperoxide (intermediate product) in this process is preceded by formation of the complex ROOH.$CoSt_2$. Fig. 17 shows that the plot of [ROOH] against u/V does not reach a maximum down to relatively small rates of flow. The absence of a maximum is indicated also by the fact that in the uncatalysed oxidation of n-decane a maximum is reached at $u = 2.5$ ml h^{-1}. Yet it can be shown that increasing the rate of initiation by adding cobalt stearate should shift the maximum to higher rates of flow. Thus if ROOH is formed and consumed by a chain mechanism (with rate constants k_2 and k_3 respectively), the rate of flow at which a maximum steady-state concentration of the hydroperoxide is reached is

$$\frac{u}{V} = \sqrt{\frac{k_3 k_3}{k_6}}\sqrt{w_i}$$

(k_6 being the recombination constant of $RO_2^{\cdot}$ radicals), and increases with increase in the rate of initiation. Calculation of the scheme of catalysed oxidation (Section II, 2) on an M-20 electronic computer, with the equilibrium

$$ROOH + CoSt_2 \rightleftarrows ROOH \cdot CoSt_2$$

maintained, showed that the steady-state concentration of ROOH does not pass through a maximum up to 88% conversion of the starting material.

Variation in the rate of supply of the starting materials affects not only the steady-state concentrations of the individual reaction products but also the proportions of the products, since change in u/V influences the steady-state concentration of the final products to a far greater extent than that of the intermediates. This effect is especially clearly developed in the oxidation of cyclohexanone by oxygen at 110°C.[15] With change in the rate of supply of cyclohexanone from 0.079 to 1.175 h^{-1} the steady-state concentration of the hydroperoxide changes from 0.298 to 0.242 mole %, i.e. by a factor of 1.2, whereas the steady-state concentration of adipic acid changes by a factor of 12.

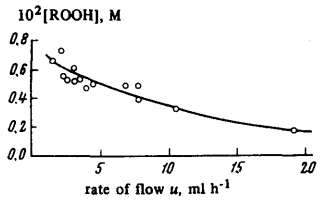


Figure 17. Dependence of steady-state hydroperoxide concentration on rate of flow in the oxidation of n-decane catalysed by cobalt stearate ($[CoSt_2]_0$ = 0.006 M) in a reaction vessel of ideal mixing at 130°C.

Furthermore, when cyclohexanone is oxidised in a gradient-free reaction vessel, the extent of oxidation of adipic acid to carbon dioxide is considerably diminished. If with 4.5 mole % of adipic acid the rate of evolution of carbon dioxide per mole of adipic acid is 0.124 mole h^{-1} under static conditions, in an open system it is only 0.032 mole h^{-1}.

In general in the consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$ increase in the rate of supply of the starting materials will enrich the mixture in the intermediate products. Thus the concentration of C in the steady state is given by

$$k_2[\bar{B}] - (k_3 + u/V)[\bar{C}] = 0, \text{ whence } \frac{[\bar{B}]}{[\bar{C}]} = \frac{(k_3 + u/V)}{k_2}.$$

With increase in u/V the ratio $[\bar{B}]/[\bar{C}]$ increases: i.e. the relative content of B in the mixture of reaction products is increased.

This conclusion may not apply to more complicated reactions, such as the oxidation of organic compounds[10]. Analysis of a process of oxidation involving chain branching by the reaction $ROOH \xrightarrow{k_3} HO^{\cdot} + RO^{\cdot}$ and quadratic recombination of radicals ($RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_6}$ products) shows that the ratio of the steady-state concentrations of the hydroperoxide (ROOH) and a product C, the latter formed from the hydroperoxide by a molecular mechanism (constant k) and consumed by a chain mechanism§ (constant k_4), is given by

$$\eta = \frac{[\overline{ROOH}]}{[\bar{C}]} = \frac{k_3 \cdot k_3 k_4 [RH]}{k k_6 (k + u/V)} + \frac{u/V}{k}$$

§ If the reaction product is not used up or is consumed by a molecular mechanism, this scheme yields a result identical with that obtained from consideration of a simple consecutive reaction.

in which k_2 is the rate constant of chain propagation $RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$. It is seen from this expression that the ratio of the steady-state concentrations increases at small rates of flow, but with further increase in u/V it falls. The maximum value of η is attained at the rate of flow

$$u/V = \sqrt{\frac{k_2 k_3 k_4 [RH]}{k_6}} - k.$$

Thus with consecutive chain reactions variation in the flow rate over a certain range may result in enrichment of the mixture with the first intermediate, and over another range enrichment with the second intermediate. The concentration ratio of intermediate and final products increases steadily, as with simple consecutive reactions[10].

With variation in the rate of supply of ethylbenzene the ratio of the steady-state concentrations of the hydroperoxide and 1-phenylethanol formed by its oxidation passes through a maximum (Fig. 18).[17] At the same time the ratio of the steady-state concentrations of the hydroperoxide and of acetophenone (AcPh) increases monotonically, as can be seen from the following data

u, ml h^{-1}	0.40	0.55	0.75	0.95	2.0	2.2
$[\overline{ROOH}]/[\overline{AcPh}]$	5.2	5.7	8.1	9.3	15	15.7

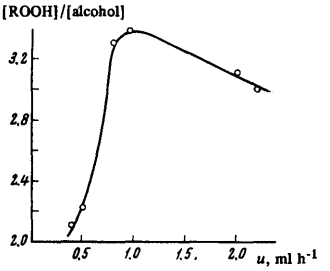


Figure 18. Dependence of ratio of steady-state concentrations of hydroperoxide [ROOH] and 1-phenylethanol on the volume flow rate of ethylbenzene to a reaction vessel with ideal mixing at 118°C.

In concluding this Section it is appropriate to mention that the maximum steady-state concentration attainable in an open system is always lower than the maximum concentration of a product under static conditions with the same process conditions. Thus in the consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ the steady-state concentration of the final product C

$$[\overline{C}] = \frac{[A_0] k_1 k_2}{(k_1 + u/V)(k_2 + u/V)}$$

is always lower than the maximum possible concentration $[C] = [A]_0$ under static conditions, and tends to it as the rate of flow diminishes. The maximum possible steady-state concentration of the intermediate product B, attainable at a rate of flow $u/V = \sqrt{k_1 k_2}$, is

$$[\overline{B}]_{max} = \frac{[A]_0 \cdot k_1}{(\sqrt{k_1} + \sqrt{k_2})^2}.$$

Yet for the maximum concentration of this product under static conditions[11] we have

$$[B]_{max} = [A]_0 \left(\frac{k_2}{k_1}\right)^{k_1/(k_2 - k_1)}.$$

Writing $k_2/k_1 = \kappa$, we find that the ratio of the maximum concentration of B under static conditions to its maximum concentration in an open system is

$$y = \frac{[\overline{B}]_{max}}{[B]_{max}} = \frac{\kappa^{\frac{\kappa}{1-\kappa}}}{(\sqrt{\kappa} + 1)^2}.$$

Hence it follows[10] that at all values of κ the function $y = y(\kappa)$ is less than unity: i.e. $[B]_{max}$ always exceeds $[\overline{B}]_{max}$.

The calculations given here are valid, of course, only for a simple consecutive reaction. The influence of further complication of the system on the ratio of the maximum concentrations in open and closed systems requires special examination.

V. DEPENDENCE OF REACTION VELOCITY ON FLOW RATE IN VESSELS HAVING IDEAL MIXING

The rate of change in the concentration of any substance in an open system, as already mentioned above, is given by

$$\frac{d[C]}{dt} = w_f + w_u - \frac{u}{V}[C]$$

In the steady state $(u/V)[C] = w_f - w_u$. Thus the product of the rate of supply of the starting materials by the steady-state concentration of a given substance gives the rate of accumulation of this substance in the reaction. In an open system, as under static conditions, the reaction velocity changes with the extent of the process.

For reactions of the first, second, and third order the reaction velocity (the rate of consumption of the starting material) is a maximum at the maximum concentration of the starting materials[46]. In this case, therefore, the maximum reaction velocity is reached with the maximum possible rates of supply of the starting materials. In practice, however, such rates are used very rarely, owing to the difficulty of isolating the reaction products from dilute solutions.

Let us examine the variation with the rate of flow in the rates of accumulation of intermediate and final products in the consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$.[8] The steady-state concentration of the intermediate product B is (see Section IV, 2)

$$[\overline{B}] = \frac{[A]_0 k_1 \cdot u/V}{(k_1 + u/V)(k_2 + u/V)}.$$

Hence its rate of accumulation

$$\frac{u}{V}[\overline{B}] = \frac{[A]_0 k_1 (u/V)^2}{(k_1 + u/V)(k_2 + u/V)}$$

increases monotonically with increase in the rate of supply of the starting materials, as in the case of the reaction $A \rightarrow B$, where B undergoes no further change.

For the final product C we have correspondingly

$$\frac{u}{V}[\overline{C}] = \frac{[A]_0 k_1 k_2 u/V}{(k_1 + u/V)(k_2 + u/V)}; \quad \frac{d(u/V\,[C])}{d(u/V)} = \frac{[A]_0 k_1 k_2 [k_1 k_2 - (u/V)^2]}{(k_1 + u/V)^2 (k_2 + u/V)^2}$$

It is seen that, when $u/V > \sqrt{k_1 k_2}$, the derivative

$$\frac{d\left(\frac{u}{V}[\bar{C}]\right)}{d(u/V)} < 0$$

and the rate of accumulation of the final product falls with increase in u/V. When $u/V < \sqrt{k_1 k_2}$, we have

$$\frac{d(u/V\,[\bar{C}])}{d(u/V)} > 0,$$

i.e. the quantity $[\bar{C}]u/V$ increases with increasing rate of supply of the starting materials. Thus the dependence of rate of accumulation of the product C on u/V passes through a maximum at $u/V = \sqrt{k_1 k_2}$. This same rate u/V corresponds to the maximum steady-state concentration of the intermediate product (Section IV, 2).

If in a consecutive reaction A → B → C the product B is formed autocatalytically from its precursor, not only the rate of accumulation of C but also that of B and even the rate of consumption of A should pass through a maximum with increase in the rate of flow[8]. An extremal dependence of the overall rate of the process and the rate of accumulation of each product on the rate of supply of the initial substances is observed in an open system whenever the kinetic curve for accumulation of the given product under static conditions is S-shaped.

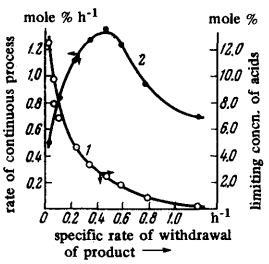


Figure 19. Dependence, on specific rate of supply of cyclohexanone during its continuous oxidation at 110°C, of: 1) steady-state concentration of adipic acid; 2) rate of accumulation of adipic acid.

In the oxidation of cyclohexanone in an open system the rate of accumulation of adipic acid first increases with increase in u/V, passes through a maximum, and then falls[15] (Fig. 19). Analogous extremal variations in the rate of consumption of hydrocarbon and of accumulation of each of the reaction products with increase in u/V have been observed also in the oxidation of n-decane at 140°C (Fig. 20).[8] It is seen from Fig. 20 that the rates of accumulation of all the products of the reaction pass through a maximum, including the rate of accumulation of the first intermediate product, the hydroperoxide. The maxima in the rates of accumulation of all the products with variation in the flow rate are displaced relative to each other, being reached at different flow rates.

With the simple consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$ as example it has been shown[10] that the maximum rates of accumulation of the individual reaction products should be observed at different values of u/V. For the accumulation of C and D we can write the differential equations

$$\frac{d[C]}{dt} = k_2[B] - (k_3 + u/V)[C] = 0; \quad \frac{d[D]}{dt} = k_3[C] - \frac{u}{V}[D] = 0.$$

Hence the rates of accumulation of these products are

$$\frac{u}{V}[\bar{C}] = \frac{k_2[\bar{B}]\,u/V}{(k_3 + u/V)}; \quad \frac{u}{V}[\bar{D}] = k_3[\bar{C}] = \frac{k_2 k_3 [\bar{B}]}{(k_3 + u/V)}$$

The maximum rate of accumulation of D is reached when

$$\frac{d}{d(u/V)}\left[\frac{[\bar{B}]}{(k_3 + u/V)}\right] = 0;$$

and the maximum rate of accumulation of C when

$$\frac{d\left[\frac{u}{V}[C]\right]}{d(u/V)} = k_2 \frac{u}{V} \frac{d}{d(u/V)}\left[\frac{[\bar{B}]}{(k_3 + u/V)}\right] + \frac{k_2[\bar{B}]}{(k_3 + u/V)} = 0.$$

At the point $d(u[\bar{D}]/V)/d(u/V) = 0$ we have $d(u[\bar{C}]/V)/d(u/V) > 0$: i.e. the maximum rate of accumulation of C is reached at higher values of u/V than is that of D. If one of the stages in the sequence or all of the stages in this process are autocatalytic, the maximum rates of accumulation of individual products are also observed at different rates of flow.

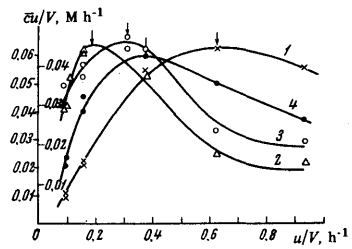


Figure 20. Dependence, on rate of supply of n-decane during its oxidation in reaction vessel of ideal mixing at 140°C, of rates of accumulation of: 1) hydroperoxides (outer scale); 2) acids (outer scale); 3) ketones (inner scale); 4) alcohols (inner scale).

As already remarked above, the maximum rate of accumulation of any final product of a simple consecutive reac- A → B → C is reached at the same rate of supply of the starting materials as is the maximum steady-state concentration of the intermediate which is the immediate precursor of the given final product (see above), independently of whether B can be consumed only by conversion into C or in more than one way. This property of an open system has yielded a possible method for determining the routes by which the final reaction products are formed.

The method consists in comparing the maximum rates of accumulation of the final products and the steady-state concentrations of the intermediates with variation in the flow rate. If these maxima are reached at the same flow rate, the intermediate can be regarded as the direct precursor of the given final product[8].

However, this method of determining the paths by which the final products are formed is not general, and requires careful analysis of the mechanism and the conditions under

which the process is conducted. Thus in the autocatalytic consecutive reaction A → B → C → D, where the reaction product B accelerates consumption of C, the maximum rate of accumulation of D and the maximum steady-state concentration of C should be reached at different values of u/V. However, some modification of the method enables the paths by which D is formed to be determined even in this case[10].

Analysis of the scheme for a chaim oxidation in the liquid phase, where the product D is formed by a chain mechanism involving free peroxy-radicals $RO_2^{\cdot}$ formed by the breakdown of B (with a rate constant k_2'), shows that the rate of accumulation of D in this case is $u[\bar{D}]/V = k_3[\bar{C}][RO_2^{\cdot}]$, or $u[\bar{D}]/V = k_3(k_2'[\bar{B}][\bar{C}]/k_6)^{1/2}$, since with quadratic recombination of radicals (rate constant k_6) we have $[RO_2^{\cdot}] = (k_2'[\bar{B}]/k_6)^{1/2}$.

Since the amount of B is affected by change in the flow rate, the maxima in the relations $u[\bar{D}]/V = f_1(u/V)$ and $u[\bar{C}]/V = f_2(u/V)$ will not coincide. However, if a substance which will ensure a sufficiently rapid rate of formation of radicals $RO_2^{\cdot}$ is added to the system together with the starting materials, so that $w_i > k_2'[\bar{B}]$, we have

$$u/V\,[\bar{D}] = k_3[\bar{C}][RO_2^{\cdot}] = \frac{k_3[\bar{C}]}{\sqrt{k_6}}\sqrt{w_i}$$

By varying the initiator concentration so that w_i remains constant with variation in the flow rate, these maxima can be made to coincide.

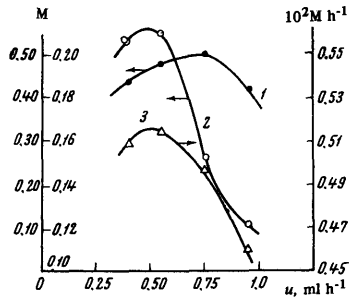
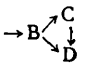


Figure 21. Dependence, on rate of supply of ethylbenzene at 118°C, of: 1) steady-state concentration of hydroperoxide; 2) steady-state concentration of 1-phenylethanol; 3) rate of accumulation of acetophenone.

The method has been tested for the oxidation of ethylbenzene[17]. (Preliminary experiments had shown that acetophenone was formed directly from 1-phenylethanol, not by decomposition of the hydroperoxide—see below.) Fig. 21 illustrates the dependence of the rates of accumulation of acetophenone and of the steady-state concentrations of ethylbenzene hydroperoxide and 1-phenylethanol on the rate of supply of ethylbenzene. The rate of initiation of chains was maintained constant to ±4% while u/V was varied from 0.096 to 0.041 h^{-1}. It is seen from Fig. 21 that the maximum rate of accumulation of acetophenone is reached at the same value of u/V as is the maximum steady-state concentration of 1-phenylethanol.

When the final product in a complicated consecutive-parallel reaction is formed by two or more parallel routes, it is also possible to establish these paths. Thus it has been shown[10], for example, that in the consecutive-parallel reaction



the maximum steady-state concentration of B is reached at the same value of u/V as is the total rate of accumulation of the products C and D.

VI. USE OF REACTIONS IN VESSELS HAVING IDEAL MIXING AS METHOD OF INVESTIGATING THE MECHANISM OF CHEMICAL REACTIONS

Study of the kinetics of reactions in vessels with ideal mixing enables the paths by which the final products are formed to be assessed from the dependence of the steady-state concentrations of the intermediate substances and the rates of accumulation of the final products on the rate of flow. However, this is not the only possibility for studying reaction mechanisms and rates of formation of products provided by open systems.

One of the greatest advantages of open systems is that the use of gradient-free reaction vessels makes it possible to study a reaction under perfectly constant experimental conditions, for variation in the conditions during an experiment makes it difficult to interpret the results. The influence of such factors as the pH of the medium, the dielectric constant, etc. is far more easily established when the reaction is conducted in an open system, where constant conditions can be maintained as long as desired.

Such systems present a considerable advantage also for the study of rapid chemical reactions. This method has been used, for example, to study the rapid interaction of iron(II) ions with sodium thiosulphate[47]. The reaction involves the intermediate formation of a violet complex. Under static conditions the coloration disappears extremely rapidly, and it is practically impossible to obtain the spectrum of this compound. Conducting the reaction in an open system with solutions of sodium thiosulphate and of an iron salt fed separately to the vessel enabled the spectrum of the intermediate complex to be obtained. At sufficiently high rates an intense violet coloration was established, which was stable with time and enabled the absorption spectrum of the complex to be recorded. The lifetime of the complex was found to be 10 s.

The attainment of steady-state concentrations when chemical reactions are conducted in gradient-free reaction vessels simplifies mathematical analysis of the set of kinetic equations describing the process. This in turn considerably facilitates the task of determining the rate constants for reactions of differing order from known concentrations of the reaction components.

1. Determination of Rate Constants for Simple Types of Reactions

The rate constants of first-order reactions in open systems can be determined quite simply[50] both from the steady-state concentration of starting material or final product (see Eqns. 12 and 13) and from the time required to reach half the steady-state concentration (Eqn. 3a). These formulae do not take into account a possible change in volume during the reaction. Yet most first-order reactions in the gas phase involve a change in volume. Use

of the formulae (13) and (12) then becomes impossible because of the inequality in the rates of withdrawal of products and supply of starting materials, so that the formula

$$k_1 = \frac{(u/V)[A]_0 - (u/V)_1[\bar{A}]}{[\bar{A}]}$$

where u/V is the rate of supply and $(u/V)_1$ the rate of withdrawal of the starting material A from the system, must be applied[51].

It is thus sufficient to know merely the speed of the gas on entering and on leaving the vessel in order to determine the rates of the process. Nevertheless, a change in volume during the process greatly increases the difficulty of studying reactions in a laminar flow system, since it is then necessary to know the law governing the change in volume throughout the length of the vessel.

As example of the determination of a first-order rate constant we can cite the gas-phase decomposition of chlorocyclohexane (A), which is accompanied by the evolution of elementary chlorine[52]. Progress of the reaction was followed from the change in concentration of chlorine. Since the process involves a change in volume, the rate of withdrawal of chlorine from the system is not equal to the rate of supply of chlorocyclohexane. The rate of change in the chlorine concentration can be written

$$\frac{d[Cl_2]}{dt} = k_1[A] - \frac{u_{Cl_2}}{V}[Cl_2]$$

where u_{Cl_2} is the space velocity of removal of chlorine from the system. After a steady-state chlorine concentration has been established, when $d[Cl_2]/dt = 0$, the constant k_1 is determined by means of the formula

$$k_1 = \frac{u_{Cl_2}}{V}\frac{[\bar{Cl}_2]}{[\bar{A}]}.$$

The value obtained for the decomposition rate constant of chlorocyclohexane was identical with that determined previously under static conditions, which indicates that reaction rate constants can be determined by this method.

A similar study has been made of the pyrolysis of ethyl acetate, which is also a first-order reaction accompanied by a change in volume[53]. The rate constant was determined over the temperature range 376–531 °C, and it was found that the activation energy varied with temperature.

The possibility of determining the rate constants of bimolecular reactions has been examined in detail for the reaction $A + B \xrightarrow{k} C$. In this case k can be determined by measuring the concentration of at least one of the substances present in the system (e.g. C), provided that the initial concentrations a_0 and b_0 of A and B in the mixture entering the vessel are known, together with the rate of supply of A and B to the system[50]. Thus if A and B enter the system with different space velocities u_A and u_B, while the reaction product is removed from the system at the rate $u = u_A + u_B$, the constant is determined by means of the formula

$$c = \frac{(V/u)\ k\ (u_A \cdot a_0 - u \cdot c)\ (u_B \cdot b_0 - u \cdot c)}{u^2}.$$

The rate constant of a bimolecular reaction in a gradient-free reaction vessel was first measured by Bodenstein[1], as already mentioned.

Use of a reaction vessel with ideal mixing facilitates the task of determining the rate constants not only of simple but also of complicated, multistage reactions, among which are consecutive, parallel, and consecutive–parallel reactions.

The individual rate constants of each process can be determined for a series of parallel reactions. In one of the simplest cases, e.g. when several parallel reactions

$$\begin{aligned} A_1 + B &\rightarrow C_1 \quad (k_1)\\ A_2 + B &\rightarrow C_2 \quad (k_2)\\ &\cdots\\ A_n + B &\rightarrow C_n \quad (k_n) \end{aligned}$$

are occurring in a system, each of the constants can be determined by conducting the process with various rates of supply of the starting materials, only the steady-state concentration of these substances being measured. In fact, the rate of change in the concentration of B is

$$\frac{d[B]}{dt} = -k_1[A_1][B] - k_2[A_2][B] - \ldots - k_n[A_n][B] - \frac{u}{V}[B] + \frac{u}{V}[B]_0. \quad (15)$$

When $d[B]/dt = 0$, this equation is converted into an algebraic equation, in which all the k_i can be determined provided that there are n such equations. If the parallel reactions take place in the gas phase and are accompanied by change in volume, the formulae for calculating the individual constants are somewhat complicated[51].

The rate constants of parallel reactions have been determined for the gas-phase decomposition of isopropyl and s-butyl chloroformates, which is accompanied by change in volume[52,53]. When the gaseous compounds are heated to high temperatures, they may undergo either substitution or decomposition with formation of alkenes; in the case of the s-butyl ester, two stereoisomeric compounds—*cis*- and *trans*-but-2-ene—can be formed. Conducting these processes in an open system has enabled the rate constants of each of the parallel stages to be determined at various temperatures.

In the case of a simple consecutive reaction of the type $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ with the same rate of supply of the starting materials, both constants can be determined from the steady-state concentrations of the initial and intermediate substances (A and B) by means of the equations¶

$$-k_1[\bar{A}] - \frac{u}{V}[\bar{A}] + \frac{u}{V}[A]_0 = 0 \quad (16)$$

$$k_1[\bar{A}] - k_2[\bar{B}] - \frac{u}{V}[\bar{B}] = 0. \quad (17)$$

If the concentration of the intermediate cannot be measured, the constants k_1 and k_2 can be determined from the steady-state concentrations of the final reaction product (C) with various rates of supply of the starting materials, by means of the formula

$$[\bar{C}] = \frac{k_1 k_2 [A]_0}{(k_1 + u/V)(k_2 + u/V)}$$

or

$$\frac{1}{u/V}\left\{\frac{1}{[\bar{C}]} - \frac{1}{[A]_0}\right\} = \frac{1}{k_1 k_2}(k_1 + k_2) + \frac{1}{k_1 k_2} \cdot \frac{u}{V}.$$

In the latter case, by plotting

$$\frac{1}{u/V}\left(\frac{1}{[\bar{C}]} - \frac{1}{[A]_0}\right)$$

against u/V, we can determine k_1 and k_2 separately.

Determination of the rate constants for all stages in a process is possible also when a common component takes

¶ Use of an analogous method under static conditions necessitates the graphical differentiation of the kinetic curves for the consumption of A and the accumulation of B, which diminishes the accuracy of the constants obtained.

part in every stage in a consecutive bimolecular reaction[54]. The possibility of determining rate constants for consecutive bimolecular reactions has been examined in detail for chlorinations represented by the scheme

$$A + B \xrightarrow{k_1} A_1$$
$$A_1 + B \xrightarrow{k_2} A_2 \text{ etc.}$$

In this case the constant k_1 can be determined from the formula

$$k_1 = \frac{u}{V \cdot a \cdot x}(1-a) \qquad (18)$$

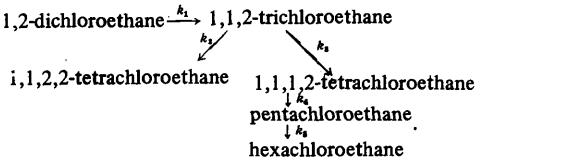
where a is the steady-state mole fraction of A in the reaction vessel, while x is the number of moles of chlorine which have reacted per mole of the initial substance A consumed. The value of x is given by the sum of the mole fractions of all the chlorinated reaction products multiplied by the appropriate coefficients:

$$x = a_1 + 2a_2 + 3a_3 + \ldots + na_n$$

The constant k_2 can be determined if the steady-state mole fractions of A and A_1 are known:

$$k_2 = \frac{u}{V} \cdot \frac{1}{a_1 x}(1-a_1-a_2). \qquad (19)$$

The above formulae (18) and (19) have been used to determine the rate constants for the chlorination of 1,2-dichloroethane at 100°C, which is represented by the scheme



The constants k_1, k_2, and k_3 were determined in the chlorination of 1,2-dichloroethane, and it was shown that 1,1,2,2-tetrachloroethane does not undergo further chlorination. The constants k_4 and k_5 were measured in the chlorination of 1,1,2-trichloroethane[55] and of 1,1,1,2-tetrachloroethane[56] under analogous conditions.

Conducting a process in open systems enables not only the rate constants but also the order of the reaction to be determined. If a reaction of the nth order with respect to some component, e.g. $nA \rightarrow B$, is conducted in an open system with different rates of supply $(u/V)_1$ and $(u/V)_2$ of the starting materials, the steady-state concentrations $[\bar{A}]_1$ and $[\bar{A}]_2$ are given by

$$k[\bar{A}]_1^n = \left(\frac{u}{V}\right)_1 ([A]_0 - [\bar{A}]_1) \qquad (20)$$

$$k[A]_2^n = \left(\frac{u}{V}\right)_2 ([A]_0 - [\bar{A}]_2) \qquad (21)$$

Dividing Eqn. (20) by (21) term by term and taking logarithms, we obtain

$$n \lg \frac{[\bar{A}]_1}{[\bar{A}]_2} = \lg \left\{ \frac{u_1}{u_2} \cdot \frac{([A]_0 - [\bar{A}]_1)}{([A]_0 - [\bar{A}]_2)} \right\},$$

the slope of the plot of $\lg([\bar{A}]_1/[\bar{A}]_2)$ against the right-hand side of this equation giving the order n of the reaction.

Determination of the order of a reaction is a far more laborious task in open systems than under static conditions, since it requires many experiments to be made, whereas under static conditions a kinetic curve with a practically unlimited number of points is obtained in one experiment. Nevertheless, in several complicated processes the order with respect to some component is better determined in open systems. Among such reactions are all those processes in which change in the composition of the product during the reaction changes the apparent order of the reaction.

Thus, for example, the order of the polymerisation of styrene in the presence of an initiator—benzoyl peroxide—has not been accurately established. From some results it has been assumed that the reaction is of the first order with respect to the monomer, whereas other results indicate an order of 1.5. Study of this process in open systems has shown[12] that the apparent order of the reaction with respect to the monomer varies from 1.18 to 1.36 depending on the composition of the reactant mixture.

A property of open systems which is among the most valuable for the study of reaction mechanisms is the possibility of investigating the reaction over a wider temperature range—both downwards and upwards—than under static conditions.

When reactions are studied in open systems, it becomes possible to conduct processes at very small degrees of conversion, which cannot be used under static conditions because of analytical difficulties. The practically unlimited volumes of gases or liquids leaving the reaction vessel in open systems make it possible to accumulate analytically detectable amounts of products even at low degrees of conversion. As a consequence, the temperature of the reaction can be considerably lowered in comparison with static conditions.

At the same time the continuous supply of starting materials to the system prevents them from being completely burned out, so that reactions in open systems can be conducted at considerably higher temperatures than under static conditions. Thus in an investigation[52] of the thermal decomposition of chlorocyclohexane in the gas phase in a flow-type reaction vessel with stirring, it proved possible to raise the temperature from 385°C (the maximum temperature at which the decomposition of this substance had been studied under static conditions) to 476°C, i.e. by almost 100 deg. Study of the decomposition of ethyl acetate in open systems over a wide temperature range enabled a change in mechanism of pyrolysis with rise in temperature to be detected[53]: at high temperatures (above 500°C) the activation energy of pyrolysis is 44 kcal mole^{-1}, but when the temperature is lowered to 376–414°C the activation energy falls to 41 kcal mole^{-1}.

The possibility of determining rate constants for simple types of reactions, as well as for parallel and consecutive reactions, is undoubtedly a merit of open systems. In most cases, however, especially for simple types of reactions, these constants can easily be determined also under static conditions.

The advantage of "open" systems over all other methods of conducting a process is shown most clearly when it is necessary to study complicated reactions. Variation in conditions during the process (e.g. change in the ionic strength of the solution, the dielectric constant, the pH, etc.) makes the determination of rate constants under static conditions extremely inaccurate, and interpretation of the results difficult. To maintain the ionic strength, pH, etc. constant under static conditions special methods are used (e.g. buffer solutions or continuous titration of the solutions during the process, which changes the volume of the system and thereby introduces additional difficulties).

Open systems enable a process to be conducted under conditions which remain unchanged for a long time, so that the reaction velocity can be measured accurately with the composition of the reaction mixture rigidly fixed. An

example is provided by the bromination of acetone under conditions of ideal mixing[57]. The rate constant of this process, determined from the scheme for a simple consecutive reaction, varies considerably with the extent of reaction, so that it was concluded that this reaction is more complicated than the scheme adopted in the literature.

2. Determination of Rates of Reactions involving Reactive Intermediates

The method described above for determining the rate constants of individual stages in parallel and consecutive reactions cannot always be used to determine the rates of chain reactions involving active intermediate species, whose concentration is often impossible to measure.

The kinetics of the accumulation of an intermediate B in consecutive chain reactions, e.g. $A \xrightarrow{RO_2^\cdot} B \xrightarrow{RO_2^\cdot} C$, in an open system is described by the equation

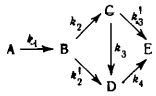
$$\frac{d[B]}{dt} = k_1[RO_2^\cdot][A] - k_2[RO_2^\cdot][B] - \left(\frac{u}{V}\right)[B] = 0. \qquad (22)$$

If the steady-state concentration of the initial substance A is known, Eqn. (22) can be used, together with the equation

$$\frac{d[A]}{dt} = -k_1[RO_2^\cdot][A] - \frac{u}{V}([A] - [A]_0) = 0 \qquad (23)$$

for the consumption of A, to determine the products $k_1[RO_2^\cdot]$ and $k_2[RO_2^\cdot]$, and hence the separate rates of formation and consumption of B for a given rate of supply of the substances.

In general, if the number of unknown rate constants exceeds the number of component concentrations which can be measured, it is impossible to determine the rates of formation and consumption of a substance from an experiment conducted at a single rate of flow. For example, the sequence of reactions



in the steady state can be described by a set of five equations with six unknown constants, and it becomes possible to determine all the constants only by conducting the reaction with several different velocities. In several cases, however, change in the rate of flow has a complicated effect on the concentration of free radicals, and separate determination of the rates of formation and of consumption of intermediates becomes impossible.

The rates of formation and consumption of products in chain reactions are now being very successfully measured by a kinetic method of labelled atoms, in which small additions of intermediates labelled with a radioactive isotope are introduced into the system[58]. However, the method is quite laborious, and involves isolation of the given intermediate from a complicated mixture of reaction products, which is often a quite difficult task. Use of the labelled atoms method in an open system[59] makes this problem slightly easier.

A new method has recently been suggested for determining the rates of formation of intermediates[60]. It consists in conducting the reaction in an open system until a steady state is established. From then a certain quantity of the intermediate, whose rates of formation and consumption are to be measured, is added to the reaction vessel together with the starting material. The bulk rate of supply of the substance to the vessel should not be varied. In this case the steady-state concentrations of the initial substance and of the branched product (and hence also the steady-state concentration of free radicals) remain unchanged, since the rate of supply of the starting materials is constant. The difference in the steady-state concentrations of the intermediate established in the two cases enables its rates of formation and consumption in the system to be determined†.

In the consecutive reaction $A \xrightarrow{RO_2^\cdot} B \xrightarrow{RO_2^\cdot} C$ the steady-state concentration of B when only the initial substance A is fed to the system is given by the equation

$$k_1[RO_2^\cdot][\bar{A}] - k_2[RO_2^\cdot][\bar{B}] - \frac{u}{V}[\bar{B}] = 0 \qquad (24)$$

but when solutions containing additions of B at concentration $[B]_0$ are supplied we have

$$k_1[RO_2^\cdot][\bar{A}] - k_2[RO_2^\cdot][\bar{B}]_1 - \frac{u}{V}[\bar{B}]_1 + \frac{u}{V}[B]_0 = 0. \qquad (25)$$

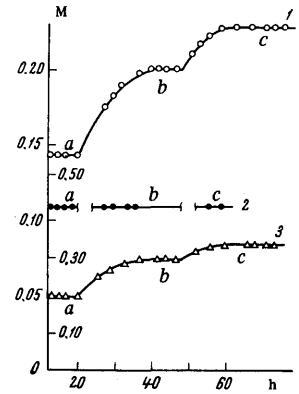


Figure 22. Oxidation of ethylbenzene in reaction vessel of ideal mixing at 118°C, with rate of flow 0.102 h^{-1}, during supply of ethylbenzene (sections a) and of 0.106 M and 0.17 M solutions of 1-phenylethanol in ethylbenzene (sections b and c). Kinetic curves for the accumulation of: 1) alcohols (outer scale); 2) hydroperoxides (inner scale); 3) ketones (outer scale).

As mentioned above, the steady-state concentrations of A and $RO_2^\cdot$ are not affected by supplying to the system a solution containing B. Solution of Eqns. (24) and (25) gives

$$\left(1 + \frac{k[RO_2^\cdot]V}{u}\right) = \frac{[B]_0}{[\bar{B}]_1 - [\bar{B}]} \qquad (26)$$

For a first-order reaction $[\bar{B}]_1 - [B]$ can be plotted against $[B]_0$, the slope giving $k_2[RO_2^\cdot]$, from which $k_1[RO_2^\cdot]$ can be calculated, as well as the ratio of the rate constants for formation and consumption of B. If B is consumed by an nth-order reaction, Eqn. (26) becomes

$$\frac{k_2[RO_2^\cdot]V}{u} = \frac{[B]_0 + [\bar{B}]^n - [\bar{B}]_1^n}{[\bar{B}]_1 - [\bar{B}]} \qquad (27)$$

† This method cannot be used if addition of the intermediate has a substantial effect on the rate of chain branching.

Use of this method to study the autoxidation of n-decane and ethylbenzene has yielded the ratios of the rate constants for interaction of $RO_2^{\cdot}$ radicals with the alcohol, the hydroperoxides, and the hydrocarbon[60-62]. For example, the rate of formation of 1-phenylethanol in the oxidation of ethylbenzene has been determined from experiments in which 0.106 M and 0.17 M solutions of the alcohol in ethylbenzene were supplied to the vessel. Fig. 22 shows that the steady-state concentrations of the alcohol (*1*) and of acetophenone (*3*) increase. The constancy of the hydroperoxide concentration (*2*) indicates that the concentration of radicals remains unchanged for all additions of the alcohol. The steady-state concentrations of 1-phenylethanol (B) obtained are plotted in Fig. 23 as $[\bar{B}]_1 - [\bar{B}]$ against $[B]_0$. From the slope of the straight line obtained it was calculated that $k_2[RO_2^{\cdot}] = 0.15\ min^{-1}$. The same method has been used to measure the rates of formation and consumption of products of the oxidation of n-decane catalysed by cobalt stearate. In this process the greater part of the alcohols, ketones, and acids were shown to be formed directly from the $RO_2^{\cdot}$ radicals[63], not by decomposition of a hydroperoxide (as occurs in the absence of a catalyst[44]).

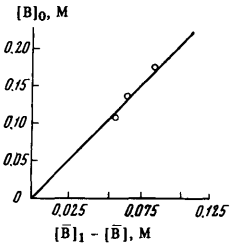


Figure 23. Dependence of difference between the steady-state concentrations of alcohols in experiments with supply of 1-phenylethanol ($[\bar{B}]_1$) and of pure ethylbenzene ($[\bar{B}]$) on concentration of 1-phenylethanol ($[\bar{B}]_0$) in solution supplied to vessel at 118°C, rate of flow 0.102 h^{-1}.

The variation in the steady-state concentration of the final product C, formed from B, with variation in the concentration of B in the solution fed to the vessel enables the rate of formation of C from B to be determined even if C is formed by several parallel routes. Actually, the rate of accumulation of C when the pure starting materials are supplied is

$$\frac{d[C]}{dt} = w_f^1 + k[RO_2^{\cdot}][\bar{B}] - \frac{u}{V}[\bar{C}] = 0$$

and when a solution of B is supplied to the system we have

$$\frac{d[C]}{dt} = w_f^1 + k[RO_2^{\cdot}][B]_1 - \frac{u}{V}[\bar{C}]_1 = 0,$$

where w_f^1 is the rate of formation of C from all products other than B. Hence the rate of formation of C from B is

$$k[RO_2^{\cdot}][B] = \frac{(u/V)([\bar{C}] + [\bar{C}]_1)[\bar{B}]}{([\bar{B}]_1 + [\bar{B}])} .$$

In this way the rate of formation of acetophenone (the final product in the oxidation of ethylbenzene in the absence of a catalyst[17,62]) from 1-phenylethanol has been calculated from the steady-state concentrations of acetophenone at various concentrations of the alcohol in the solution fed to the vessel, and oxidation of 1-phenylethanol has been shown[62] to be the only route by which the ketone is formed during the oxidation of ethylbenzene.

The mixture of reaction products often contains not only various functional derivatives but also a large number of isomeric products differing not only in the structure of the carbon skeleton but also in the position of the functional group in the molecule. When a reaction is conducted under static conditions it is extremely difficult to determine the rates of formation and consumption of each isomer, primarily because each such isomer must be isolated from the complicated mixture of reaction products. Conducting the process in an open system enables the rates of consumption of each of the isomers to be determined by analysing the total content of isomers in the system[64,65].

Let various isomeric products B_1, B_2, ..., B_n be formed in a reaction. It is required to determine the rate constant for consumption of a component B_K. Then for the total rate of accumulation of the isomers we have

$$\frac{d[B]}{dt} = \sum_{j=1}^{n} k_j[\bar{A}_j] - \sum_{\substack{i=1 \\ (i\neq k)}}^{n} k_i[RO_2^{\cdot}][\bar{B}_i] - k_k[RO_2^{\cdot}][\bar{B}_k] - \frac{u}{V}\sum_{\substack{i=1 \\ (i\neq k)}}^{n}[\bar{B}_i] - \left(\frac{u}{V}\right)[\bar{B}_k] = 0 \qquad (28)$$

When the isomer B_K is fed to the system at a concentration $[B_k]_0$, the steady-state concentrations of all isomers other than B_k remain unchanged, and the total accumulation of isomers will be described by the set of equations

$$\frac{d[B]}{dt} = \sum_{j=1}^{n} k_j[\bar{A}_j] - \sum_{\substack{i=1 \\ (i\neq k)}}^{n} k_i[RO_2^{\cdot}][\bar{B}_i] - k_k[RO_2^{\cdot}][\bar{B}_k]_1 + \frac{u}{V}\sum_{\substack{i=1 \\ (i\neq k)}}^{n}[\bar{B}_i] - \frac{u}{V}[\bar{B}_k]_1 + \frac{u}{V}[B_k]_0 = 0 . \qquad (29)$$

Subtracting Eqns. (28) from (29), we obtain

$$-k_k[RO_2^{\cdot}]([\bar{B}_k]_1 - [\bar{B}_k]) - \frac{u}{V}([\bar{B}_k]_1 - [\bar{B}_k]) + \frac{u}{V}[B_k]_0 = 0$$

$$k_k[RO_2^{\cdot}] = \frac{u}{V}\frac{-[\bar{B}_k]_1 + [\bar{B}_k] + [B_k]_0}{[\bar{B}_k]_1 - [\bar{B}_k]} = \frac{u}{V}\left\{-1 + \frac{[B_k]_0}{[\bar{B}_k]_1 - [\bar{B}_k]}\right\}$$

but

$$[\bar{B}_k]_1 - [\bar{B}_k] = \sum_{\substack{i=1 \\ (i\neq k)}}^{n}[\bar{B}_i] + [\bar{B}_k]_1 - \sum_{\substack{i=1 \\ (i\neq k)}}^{n}[\bar{B}_i] - [\bar{B}_k] = [\bar{B}_1] - [\bar{B}]$$

where $[\bar{B}]_1$ and $[\bar{B}]$ are the total concentrations of all the B isomers. Hence

$$k_k[RO_2^{\cdot}] = \frac{u}{V}\left\{-1 + \frac{[B_k]_0}{[\bar{B}]_1 - [\bar{B}]}\right\} .$$

The method was used to determine the reactivities of the isomeric decanols[65] in the oxidation of n-decane at 140°C. After a steady-state concentration of the alcohols had been established with pure n-decane supplied to the vessel (Fig. 24, curve *1*, section *1*), the supply was begun of n-decane containing 0.205 M decan-2-ol. After a new steady-state had been established (straight line *1*, *2*), the supply of decan-2-ol was terminated, and the supply was begun of a similar solution of decan-4-ol (straight line *1*, *3*), followed by decan-5-ol (*1*, *4*).

Since the steady-state concentrations of the total alcohols were the same with all three alcohols supplied to the

vessel, it could be concluded that all the decanols had the same reactivity towards the $RO_2^{\cdot}$ radical.

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The purpose of the present review was to examine the kinetics of reactions occurring in vessels having ideal mixing, and the opportunities which such systems present for studying the mechanism of complicated chemical reactions. Among a large amount of published information, therefore only those papers have been considered which make it possible to formulate or substantiate certain general features of open systems.

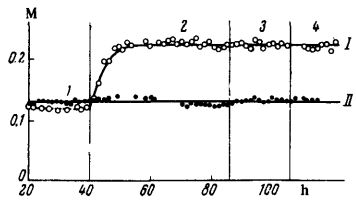

Figure 24. Steady-state concentrations of alcohols (I) and hydroperoxides (II) during the oxidation of n-decane in an open system at 140°C with a rate of flow of 0.0027 min^{-1}, during supply of: 1) n-decane containing no alcohol; 2) 0.205 M solution of decan-2-ol in n-decane; 3) 0.205 M solution of decan-4-ol in n-decane; 4) 0.205 M solution of decan-5-ol in n-decane.

Investigation of reaction kinetics in vessels having ideal mixing enables very important conclusions to be reached for the selection of reaction conditions for particular processes. Thus if the rate of accumulation of a product passes through a maximum, the maximum rate of the process can be permanently maintained by conducting it in vessels of ideal mixing. In this case the process is more suitably conducted in an open system than under static conditions[18,66].

Sometimes it is important to vary the reaction conditions during a process in order to obtain maximum yields, and this can be done especially conveniently by conducting the reaction in several vessels of ideal mixing connected in series. This procedure often enables the efficiency of a process to be increased considerably[66-70]. For example, in the sequence of processes

$$A + B \rightarrow X$$
$$X + B \rightarrow Y$$

represented in particular by chlorination, the product X is obtained in highest yield if the volumes of all the reaction vessels are the same. If primary and secondary products are formed by two parallel reactions of different order

$$2A + B \rightarrow X + Y$$
$$A + B \rightarrow Z$$

the highest yield of X is obtained by steadily increasing the volume from one reaction vessel to the next[18].

Most complicated reactions (consecutive and consecutive-parallel) involve many stages, each characterised by a definite activation energy, so that certain temperatures are required for the reactions. The possibility of varying the temperature during a process may lead to a very considerable increase in the yields.

The effect of variation in temperature has been demonstrated[18] for a model reaction represented by the scheme

$$\begin{array}{ccccc} A & + & B & \xrightarrow{2} & X \xrightarrow{4} Y \\ \downarrow 1 & & & & \downarrow 3 \\ P & & & & Q \end{array}$$

occurring in two reaction vessels of ideal mixing connected in series, Y being the required product. It was shown by calculation that, with the same temperature in the two reaction vessels, the yield of the final product cannot exceed 20-25%, whereas maintaining different temperatures in the two vessels makes it possible to increase the yield to 60%, i.e. by factors of 2.5-3.[18]

Another example of the favourable effect of change in temperature during a process is the catalytic oxidation of sulphur dioxide to sulphur trioxide[68,69]. If a definite degree of conversion (e.g. 97%) is specified, and the reaction is conducted in several vessels of ideal mixing connected in series and maintained at different temperatures, the quantity of catalyst used can be considerably diminished. In one reaction vessel of ideal mixing at 447.6°C the consumption of catalyst with 97% conversion is 0.633 m^3 h $kmole^{-1}$. If, however, the process is conducted in two series-connected reaction vessels, so that 92% conversion is achieved in the first vessel at 480°C, while in the second vessel complete oxidation of the dioxide to sulphur trioxide occurs at 447.6°C, the consumption of catalyst per kilomole of sulphur dioxide per hour with an overall degree of conversion of 97% is only 0.0577 m^3, i.e. one-eleventh.

In several cases it is extremely useful to conduct polymerisation processes in open systems. The constancy of the monomer concentration with time in an open system should lead to a narrower molecular-weight distribution[14,70], but, on the other hand, the unequal residence times of the polymeric species in the reaction zone tends to broaden the molecular-weight distribution. Which of these factors predominates will depend on the lifetime of the growing polymer chain.

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Institute of Chemical Physics,

USSR Academy of Sciences, Moscow

U.D.C. 547.298.4

Synthesis of Thioamides

K.A.Petrov and L.N.Andreev

Exhaustive data are given on methods for the synthesis of thioamides, which have now found wide application in synthetic practice, in medicine, biology, and analytical chemistry, in the foodstuffs and metallurgical industries, and in other fields. Attention is paid mainly to methods for preparing thioamides from nitriles and amides and by the Willgerodt-Kindler reaction. This is the first review of the synthesis of thioamides to be published in the Soviet literature. The list of references contains 378 items.

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INTRODUCTION

Thioamides are reactive compounds which, because of the diversity of their chemical properties, find wide application in technology[1-6], in agriculture[7-12], and in synthetic practice and medicine. They are used as vulcanisation accelerators[13-15], additives to lubricating oils, corrosion-inhibitors for metals[16-19], flotation agents[1-6], insecticides and fungicides, preservatives[20-26], medicinals for the treatment of poisoning by salts of heavy metals, starting materials for the preparation of certain vitamins (e.g. B_1), and other pharmaceutical preparations[26-38].

Thioamides have been studied in detail: more than 400 representatives of this group have been synthesised, and about 500 papers and patents have been published. However, this information is scattered among many periodicals, and is difficultly accessible. The Soviet literature contains no review papers on the chemistry of thioamides, apart from a publication on the use of thioacetamide to replace hydrogen sulphide[39] in the analysis of metals. The foreign literature contains publications of a review character[40-45], but they are either out of date or incomplete. These are the reasons for the publication of the present review.

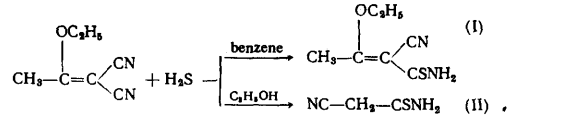
1. PREPARATION OF THIOAMIDES BY THE REACTION OF NITRILES WITH HYDROGEN SULPHIDE

Various method of preparation have been suggested for thioamides. The most convenient of them is based on the reaction of nitriles with hydrogen sulphide, since it uses readily available materials and there are practically no by-products[46-70]:

$$RCN + H_2S \rightarrow RCSNH_2$$

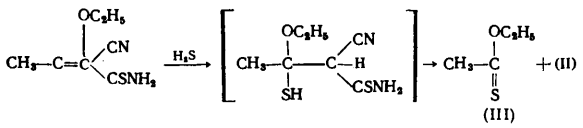
As early as 1841 the first member of the group—thiobenzamide—was obtained by this method[71]. The reaction between nitriles and hydrogen sulphide is usually conducted in various solvents and in the presence of amines, both of which influence the yield of thioamides. Among solvents which have been used are ethanol (aqueous or absolute)[72-79], aromatic hydrocarbons, dioxan, acetone[51-53,80], chloroform[81], pyridine[82,83], and in some cases water[80]. The nitrile solution was saturated with hydrogen sulphide usually at 0°C or room temperature (sometimes at 60°C [73]), a high concentration of hydrogen sulphide promoting better formation of thioamides[73]. After saturation the reaction mixture was either left at room temperature for a few days, or heated at 80–100°C,[84,85] sometimes at 100–150°C, for 6–10 h.

In isolated cases the solvent used has a substantial influence on the character of the products. Thus 1-ethoxyethylidenemalononitrile is able to give various reaction products with hydrogen sulphide depending on the solvent[86]: in benzene α-cyano-β-ethoxythiocrotonamide (I) is formed, whereas in ethanol cyanothioacetamide (II) is obtained:



The difference in the course of the reaction is explained by the differing solubility of the product (I) (formed initially

in both cases), which is insoluble in benzene and is precipitated, whereas it dissolves slightly in hot alcohol and reacts with hydrogen sulphide:



Ammonia, diethylamine, triethylamine, trishydroxyethylamine, and alkali-metal and ammonium hydrogen sulphides are used as catalysts[84,87,88]. When primary and secondary amines are used, mono- and di-substituted thioamides respectively are formed[49,50,89,90]. Hydrogen sulphide adds to nitriles especially readily in the presence of pyridine and of triethylamine[82,83].

Under otherwise similar conditions†, the yield of a thioamide depends on the nature of the nitrile: aliphatic nitriles usually add hydrogen sulphide with greater difficulty than do aromatic nitriles. The yields of aliphatic thioamides are increased by conducting the reaction at elevated temperatures and pressures. In the case of aromatic nitriles the yields are greatly affected by substituents in the aromatic ring: thus under identical conditions yields were obtained of 100% *o*-chlorothiobenzamide, 95% phenylthioacetamide, 94% thiobenzamide, 90% *p*-methoxythiobenzamide, 86% thionicotinamide, 81.5% *p*-aminothiobenzamide, 80% *p*-acetamidothiobenzamide, 70% *p*-ethylsulphonylthiobenzamide, 70% 3,4-dimethoxythiobenzamide, 65.5% thiopicolinamide, 60.5% dithioterephthalamide, and 48.5% *p*-chlorothiobenzamide[91].

The nature of the nitrile influences not only the yield of thioamide but also the reaction velocity. In the preparation of aromatic thioamides from benzonitriles containing various substituents in the ring, the following relative reaction velocities were obtained at 60°C and 1.75 atm (rate of addition of hydrogen sulphide to benzonitrile itself taken as 100): *m*-bromo 831, *p*-iodo 518, *p*-chloro 493, *p*-bromo 451, *p*-methyl 51.9, and *p*-methoxy 41.6.[92]

The action of hydrogen sulphide on dinitriles under the same conditions yields bisthioamides. Cyanogen reacts with hydrogen sulphide in the presence of bases to form dithio-oxamide (rubeanic acid $C_2H_4N_2S_2$)[58,92-100]. The reaction is conducted by saturating alcohol with the gaseous reactants or by mixing cyanogen with liquid hydrogen sulphide[27,58,92,100], the latter component being taken in excess in both cases. Cyanothioformamide is formed as an intermediate in the reaction[58], and has been isolated by carrying out the reaction in alcoholic solution with excess of cyanogen[97]. Sometimes potassium hydrogen sulphide[96] or the sodium compound[93,94,100] is used instead of hydrogen sulphide.

Dithio-oxamide has been obtained also by treating ethyl cyanoformimidate NC.C(:NH).OC_2H_5 or diethyl oxalyldiimidate C_2H_5O.C(:NH).C(:NH).OC_2H_5 with hydrogen sulphide in the presence of bases[101]. It has been proposed to obtain rubeanic acid on an industrial scale by passing a mixture of cyanogen and hydrogen chloride with stirring into an alkaline aqueous solution (pH 7–9) of sodium hydrogen sulphide at temperatures below 50°C:[93]

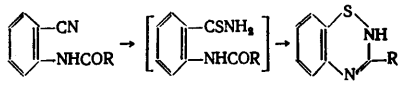
$$(CN)_2 + 2H^+ + HS^- \rightarrow H_2NCSCSNH_2.$$

No secondary products are formed in this case, unlike the process considered earlier. The initial mixture of cyanogen and hydrogen chloride is obtained by the interaction of chlorine and hydrogen cyanide at a high temperature in tubes filled with wood charcoal[93].

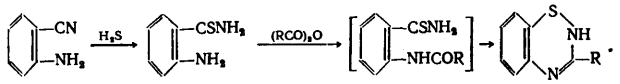
The reaction between a nitrile and hydrogen sulphide can be accomplished also in the absence of a solvent, by using the liquid reactants under pressure[85,102]. Hydrohalic acids[103] or an aluminosilicate[102] are used as catalyst in this case, besides amines. When liquid hydrogen sulphide and a liquid nitrile are used, the reaction is conducted at 50–60°C, a high yield of the thioamide being obtained. In the presence of an aluminosilicate catalyst the reaction between nitriles and hydrogen sulphide takes place under considerably more severe conditions (249–260°C)[102,104].

Under pressures of ~ 8500 atm hydrogen sulphide adds to nitriles at 80–100°C even in the absence of catalysts[85]. Thus acetonitrile and hydrogen sulphide at 80°C give thioacetamide (83%) and a certain quantity of by-products, mainly diethyl trisulphide. The temperature of the reaction must be carefully controlled, since hydrogen sulphide already acts as a reducing agent at 125–150°C.

Several nitriles, e.g. those of alanine, glycine, and *N*-acylanthranilic acids tend to cyclise when an attempt is made to prepare thioamides from them[105]. When an acylaminobenzonitrile is treated with hydrogen sulphide, ring closure occurs with the formation of thiadiazines[105]:

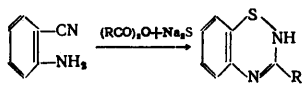


where R = CH_3, C_2H_5, $CH(CH_3)_2$, or C_4H_9. The same heterocycle can be obtained from the nitrile of unacylated anthranilic acid by treating with the anhydride of a carboxylic acid its reaction product with hydrogen sulphide (*o*-aminothiobenzamide):

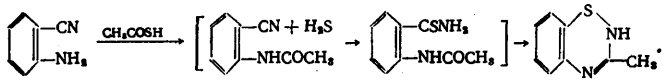


When the reaction is conducted in alcoholic–ammoniacal solution, too, cyclic products are formed. In the presence of an amine instead of ammonia an acyclic product can sometimes be isolated. Thus a small quantity of the non-cyclic thioamide of *N*-acetylanthranilic acid has been isolated from the reaction mass resulting from the interaction of *o*-acetamidobenzonitrile with hydrogen sulphide in the presence of trishydroxyethylamine; even in this case, however, the main product of the reaction was a cyclic thioamide.

The action of sodium sulphide and the anhydride of a carboxylic acid on an amino-nitrile gives a good yield also of the corresponding thiadiazine[105]:



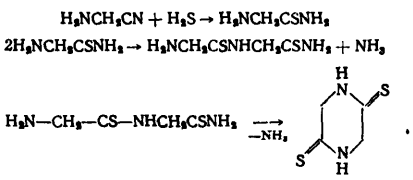
The reaction is conducted in sealed tubes at 100°C. Cyclic thioamides have been obtained also by interaction between *o*-amino-nitriles and thiolic acids in acid medium under pressure[105]:



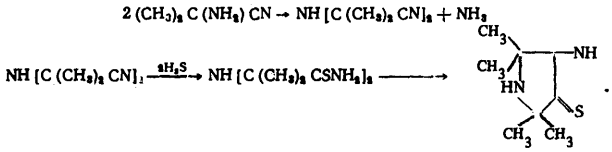
Cyclisation occurs also when hydrogen sulphide acts on aminoacetonitrile or α-aminopropionitrile in ammoniacal alcoholic solution containing ammonium sulphate, with the formation respectively of 2,5-dithionopiperazine and 3,6-dimethyl-2,5-dithionopiperazine respectively, but the

†The course of the reaction is greatly influenced by, for example, the degree of reagents and solvents.

yield is low in both cases. It is assumed that the normal thioamide is formed initially, and ammonia is eliminated from two molecules thereof with ring closure‡:

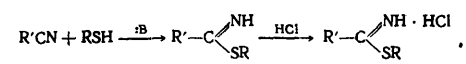


α-Aminopropionitrile reacts with hydrogen sulphide under the above conditions to form mainly aminobispropionitrile. Other α-amino-nitriles do not give dithionopiperazines at all on reaction with hydrogen sulphide. Thus α-aminoisobutyronitrile gives under the same conditions a crystalline product $C_7H_{14}N_2S$, for which the structure 2,2,4,4-tetramethyl-5-thionoimidazoline was proposed:

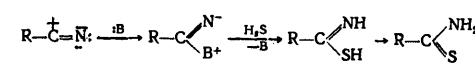


This scheme is supported by the fact that iminodi-isobutyronitrile on treatment with hydrogen sulphide yields the same cyclic product. 2-(*N*-Acetylsulphanilamido)benzonitrile on treatment with hydrogen sulphide in pyridine at 100°C gives the normal, acyclic thioamide[106].

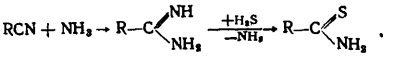
An interesting variant of the reaction of hydrogen sulphide with nitriles is that of perfluoroalkylnitriles with thiols and hydrogen sulphide. Perfluoronitriles add thiols in the presence of amines to form perfluorothioimides, from which perfluoroalkylthioamides and dithiocarboxylic esters are formed by the action of hydrogen sulphide[107]:



The mechanism of the reaction of nitriles with hydrogen sulphide has not been adequately studied. With a tertiary amine as catalyst this reaction is assumed to go according to the scheme[44]



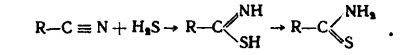
If the reaction is catalysed by a primary or a secondary amine or by ammonia, it is supposed that an amidine is formed initially, and interacts with the hydrogen sulphide to give the thioamide:



There is some indication that amidines could be isolated[89] and that they are converted into thioamides by the action of hydrogen sulphide (see below). However, these schemes probably represent only secondary reactions between hydrogen sulphide and nitriles in the presence of amines. Such reactions include also the formation of imidic esters when alcohols are used as solvent, especially as, like imides, these compounds are converted into thioamides by the action of hydrogen sulphide.

‡The interaction of thioamides with primary amines is known to liberate ammonia and involve ring closure. In the present case one thioamide molecule reacts as a primary amine, while the other acts as a thioamide.

It may be postulated that hydrogen sulphide adds directly to nitriles to form thiolomides, which then isomerise into thioamides:



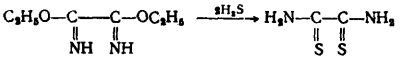
Such an assumption is supported by the fact that hydrogen sulphide reacts with nitriles at elevated temperatures and pressures to form thioamides even in the absence of amines. The role of amines as catalysts appears in the formation with hydrogen sulphide of hydrogen sulphides, which, because of the greater polarity of the bond, add to nitriles considerably more easily than does hydrogen sulphide itself.

2. PREPARATION OF THIOAMIDES BY THE REACTION OF AMIDINES, AMIDOXIMES, AND IMIDIC ESTERS WITH HYDROGEN SULPHIDE

As shown earlier, amidines and imidic esters§ are intermediates in the preparation of thioamides from nitriles and hydrogen sulphide. Therefore the reactions under consideration can be regarded as variants of the reaction of nitriles with hydrogen sulphide. They involve the intermediate addition of hydrogen sulphide at the multiple bond in the imino-compounds with formation of unstable products, which are then converted into the thioamides.

Both unsubstituted[117,118] and substituted[118-123] thioamides have been obtained by these methods. The following dithio-oxamides (percentage yields in parentheses)—*NN'*-dibutyl (70), *NN'*-diethyl (45), *NN'*-bis-3-methoxypropyl (60), and *NN'*-bis-2-hydroxyethyl (8.5)—have been isolated by saturating alcoholic solutions of the oxamidine derivatives with hydrogen sulphide[123]. *N*-Substituted thioamides are obtained also by heating *N*-substituted amidines with hydrogen sulphide at 100°C.[124] Hydrogen sulphide acts on *NN*-diphenyloxamidoxime $(C_6H_5)_2N.CO.C(:NOH).NH_2$ in ammoniacal solution to give the corresponding thioamide[125] $(C_6H_5)_2N.CO.CS.NH_2$

An interesting example of the use of imidic esters to obtain thioamides is the preparation of dithio-oxamide by the reaction of hydrogen sulphide with ethyl oximidate, which is readily formed from cyanogen chloride and ethanol, the yield of the thioamide being 90%:[101]

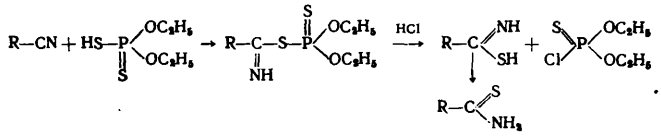


3. PREPARATION OF THIOAMIDES BY THE REACTION OF NITRILES WITH THIOPHOSPHORIC ACIDS AND THIOAMIDES

A variant of the reaction of nitriles with hydrogen sulphide is the addition of thiophosphoric acids and thioamides to nitriles. These two groups of reagents serve in such cases as sources of hydrogen sulphide. *OO'*-Diethyl hydrogen dithiophosphate has been used as the thio-

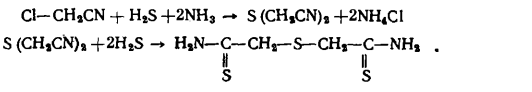
§Imidic esters are easily obtained by saturating a dry equimolecular mixture of the nitrile and the alcohol with dry hydrogen chloride[108-116].

phosphoric acid¶. The addition product is cleaved at the sulphur-phosphorus bond:

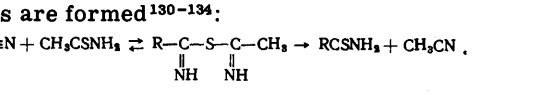


The yield of thioamides reaches 50–90%.[128]

Chlorothioacetamides, inaccessible by other methods, can be obtained[44,129]. In their synthesis, e.g. by the addition of hydrogen sulphide to chloroacetonitrile in the presence of ammonia, a sulphide is first formed, and is then converted into a bisthioamide[128]:

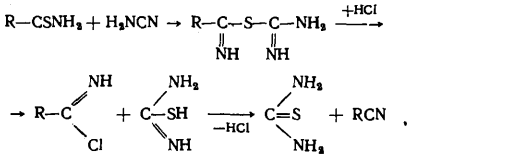


The reaction of nitriles with thioacetamide involves an intermediate stage in which mixed anhydrides of thioimidic acids are formed[130–134]:



When the low-boiling acetonitrile is distilled off, the equilibrium is shifted to the right, and good yields (63–87%) are obtained of a thioamide containing more atoms than the original. Benzonitrile reacts less smoothly with *N*-substituted thiobenzamides.

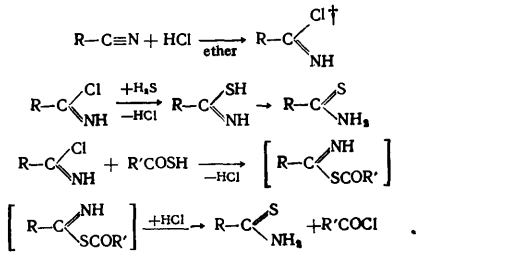
Unsubstituted thioamides react with cyanamide in warm alcoholic solution, giving a good yield of thiourea:



Interaction of these reactants in cold alcoholic solution in the presence of a mineral acid forms in good yield a salt of thiodiformamidine $NH_2C(:NH)SC(:NH)NH_2$. The same product can be obtained by the reaction of thiourea with cyanamide.

4. PREPARATION OF THIOAMIDES BY THE REACTION OF IMIDOYL CHLORIDES WITH HYDROGEN SULPHIDE AND THIO-ACIDS

Thioamides are formed[135] by the reaction of nitriles with hydrogen chloride and hydrogen sulphide or a thioacid:

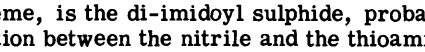


¶ For the preparation of dithiophosphates see Refs. 126 and 127.

†Doubt has recently been cast on the formation of imidoyl chlorides in this way: formation of a complex of the nitrile with hydrogen chloride is regarded as more probable[136].

These reactions can likewise be regarded as a variant of the addition of hydrogen sulphide to nitriles, distinguished by the use of hydrogen chloride instead of ammonia as catalyst. Other hydrohalic acids also catalyse the interaction of hydrogen sulphide with nitriles: thuse use of hydriodic and hydrobromic acids as catalysts for the reaction conducted in sealed tubes at 32–50°C gave yields of thioamides of 51–93% with various nitriles[103].

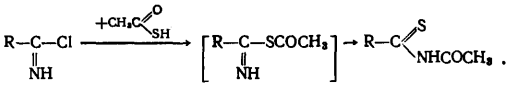
Another product of the reaction, besides those given in the scheme, is the di-imidoyl sulphide, probably formed by reaction between the nitrile and the thioamide:



The relative proportions of thioamide and di-imidoyl sulphide depend on those of the reactants: the more nitrile is present, the higher the yield of the di-imidoyl sulphide.

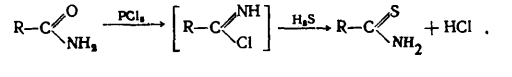
The yield of a thioamide depends on the nature of the thiolic acid and the nitrile, under otherwise similar conditions. The yield of thiobenzamide was 75% when thioacetic acid was used, 100% with thiobenzoic acid; on the other hand, interaction of *p*- and *m*-nitrobenzonitrile with acetothiolic acid gave 40% and 6% yields respectively of thiobenzamide derivatives. Some nitriles, e.g. *p*-tolunitrile and naphthonitrile, give hardly any thioamide under these conditions. A by-product in the preparation of thiobenzamide was dibenzimidoyl sulphide $C_6H_5C(:NH)SC(:NH)C_6H_5$, which is formed in good yield when benzonitrile is treated with thioacetic acid. Thiobenzoic acid gives less by-products than does thioacetic acid.

When thioacetic acid is used, an *N*-acetylthioamide may be formed as a by-product, probably by isomerisation of an intermediate product[137–139]:

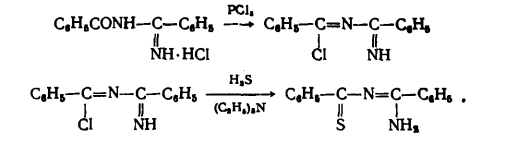


This rearrangement can be avoided by conducting the process at room temperature.

A somewhat similar method is the reaction of amides with phosphorus pentachloride and hydrogen sulphide in an inert solvent[81,140,141], in which thioamides are formed. Imidoyl chlorides are also formed as intermediates in this case:

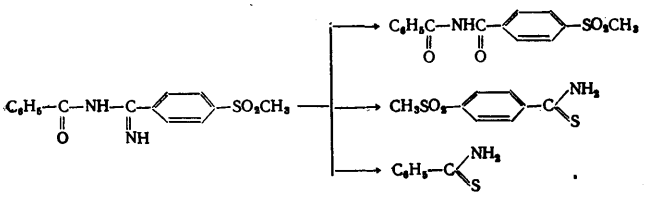


When amides containing hydroxy- and amino-groups are used, these groups are protected by treatment with toluenesulphonyl chloride. This method has been used for the preparation of thiophenacetin *p*-$C_2H_5OC_6H_4NHCSCH_3$, *p*-acetylthioacetanisidine *p*-$CH_3COC_6H_4NHCSCH_3$, *p*-phenylene-*NN'*-bisthioacetamide *p*-$CH_3CSNHC_6H_4NHCSCH_3$, and thioacetamide-trimethylpyrogallol. *N*-Thiobenzoylbenzamidine has been prepared from *N*-benzoylbenzamidine[81]:

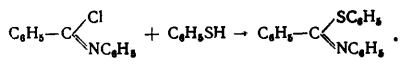


N-Thiobenzoylanisoylamidine and *N*-thiobenzoyl-*p*-chlorobenzamidine have been obtained in the same way, in yields of 48% and 26% respectively[81]. However, three products

were obtained from *N*-benzoyl-*p*-methylsulphonylbenzamidine, owing to cleavage and hydrolysis:

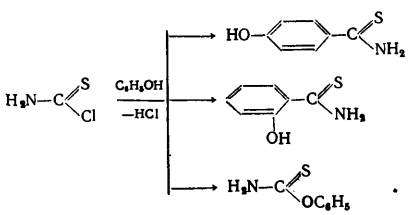


The action of arenethiols on imidoyl chlorides yields isothioamides (thiolimidic esters):



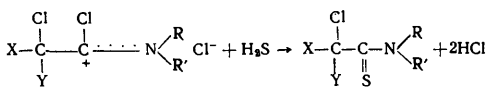
p-Tolyl *N*-*p*-tolylthiobenzimidate has been obtained from *N*-*p*-tolylbenzimidoyl chloride and toluene-*p*-thiol[141].

In several cases thiocarbamoyl chlorides are used for the synthesis of such compounds. Thus the reaction of thiocarbamoyl chloride with phenol has yielded thiosalicylamide, *p*-hydroxythiobenzamide, and phenyl thiocarbamate[141]:

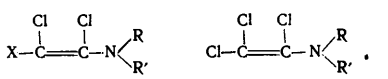


Analogous methods have been used to obtain *N*-thioacylthiocarbanilic esters[142], di-imidoyl sulphides[143,144], and several other derivatives[145].

The reaction of imidoyl chlorides with hydrogen sulphide in many cases enables thioamides to be obtained which are difficultly accessible by other methods. Thus α-chlorothioacetamides are obtained from α-chloroiminium chlorides and hydrogen sulphide[146]:

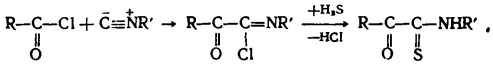


Iminium chlorides have been obtained by the addition of hydrogen chloride to 1,2-dichloro- and 1,2,2-trichlorovinylamines:



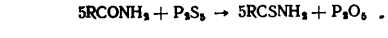
The iminium chlorides used for the preparation of trichlorothioacetamide were formed by the addition of chlorine to the above chlorovinylamines. Iminium chlorides are prepared also by the action of carbonyl chloride on *NN*-disubstituted amides of carboxylic acids.

Difficultly accessible *N*-substituted α-oxothioamides have also been prepared by the reaction of imidoyl chlorides[147,148]:

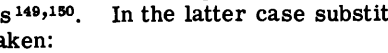


5. PREPARATION OF THIOAMIDES BY THE REACTION OF AMIDES WITH PHOSPHORUS PENTASULPHIDE

The interaction of amides of carboxylic acids with phosphorus pentasulphide involves exchange of oxygen for sulphur with formation of thioamides:

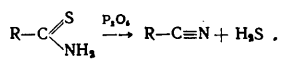


This method, first proposed in 1878, is among the most frequently used for obtaining unsubstituted and substituted thioamides[149,150]. In the latter case substituted amides must be taken:



where R, R′ = H, Alk, Ar.

When unsubstituted amides are used, nitriles are obtained as by-products, pr bably owing to decomposition of the resulting thioamide under the influence of phosphorus pentoxide[151,152]:

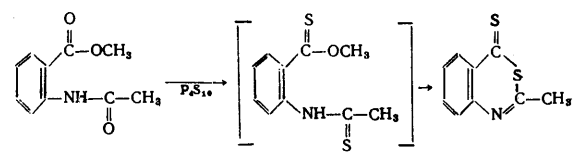


This side-reaction is sometimes so rapid that the amide is converted—not into the thioamide—but into a good yield of the nitrile[153]. Side-reactions go less vigorously with secondary[48,153-156] and tertiary[73] amides; aromatic amides react more smoothly than do aliphatic amides.

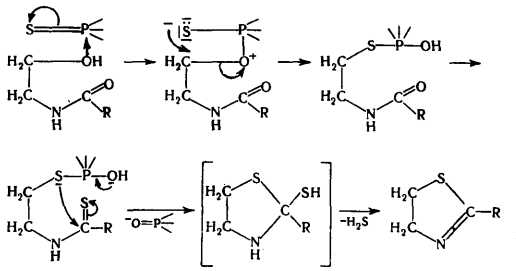
Various thioamides have been obtained by this method[157-179]. The process is conducted with heating, mostly in benzene, toluene, xylene, and tetralin; tetrahydrofuran, dioxan, and other ethers are also used as solvents. The reactions between phosphorus pentasulphide and amides are very rapid, being complete in a few minutes[150].

If the reaction between an amide and phosphorus pentasulphide is conducted in the presence of a primary or a secondary amine, *N*-mono- and *NN*-di-substituted thioamides can be obtained under suitable conditions. In this way *N*-substituted and *NN*-di-substituted thioformamides have been obtained by a one-stage process[180].

Depending on the amount of phosphorus pentasulphide taken, diamides can yield either mono- or bis-thioamides. For example, with a molar ratio of 2,4-diacetamidotoluene to phosphorus pentasulphide of ~ 2 : 1 a mixture of mono- and bis-thioamides (7 : 2) is formed[181]. Similarly, *N*-phenyloxamide yields the corresponding monothio- and dithio-compounds $C_6H_5NHCOCSNH_2$ and $C_6H_5NHCSCSNH_2$,[154] where further treatment of the former compound with phosphorus pentasulphide converts it into the latter, *N*-phenyldithio-oxamide. Oxanilides $C_6H_5NHCOCONHC_6H_5$ behave in the same way. The preparation of ethyl thio-oxanilate $C_6H_5NHCSCOOC_2H_5$ showed that the ester group does not influence the results of the reaction[154,182,183]. An exception to this rule is the reaction of methyl *N*-acetylanthranilate with phosphorus pentasulphide, accompanied by replacement of oxygen by sulphur in both amide and ester groups with cyclisation of the product to 3,4-dihydro-2-methylbenzo-3,1-thiazine-4-thione:

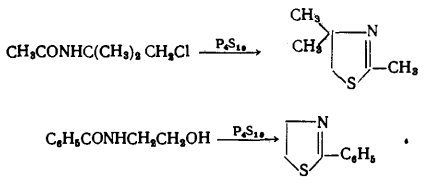


Formation of a thiazoline by the action of phosphorus pentasulphide of an *N*-2-hydroxyethylbenzamide is represented by the scheme[184,185]



The yield of thioamides obtained by treating substituted benzamides with phosphorus pentasulphide is greatly affected by the nature of the substituents. Thus treatment of *m*- and *p*-nitrobenzanilides with phosphorus pentasulphide in boiling xylene gives 70–90% yields of the corresponding thioamides; under the same conditions the aminobenzanilides form thioamides in only 5% yield[169]. Similar results were obtained in toluene, reaction being rapid with the nitro-derivatives and slow with the amino-derivatives. No thioamide is formed when *pp'*-dinitrooxanilide is treated with phosphorus pentasulphide in xylene for 7 h, the nitro-groups undergoing reduction to amino-groups[186]. However, no systematic study has yet been made of the influence of substituents on the yield of thioamides.

The reaction of phosphorus pentasulphide with certain *N*-substituted amides (containing a functional group in the β-position with respect to the nitrogen atom) is sometimes accompanied by cyclisation[184,187]:



In this example formation of 2-phenylthiazole is accompanied by that of a cystamine derivative $(C_6H_5CONHCH_2CH_2S)_2$.[184]

With hydantoins phosphorus pentasulphide yields thiohydantoins, whose specific action is weaker and less prolonged than that of the corresponding derivatives of barbituric acid[188].

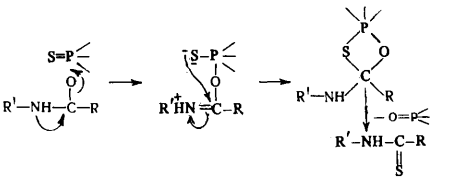
The yield of thioamides obtained from amides and phosphorus pentasulphide is appreciably increased by the presence of oxides or carbonates of alkaline-earth metals[189]; potassium sulphide also has a favourable effect[165]. In the latter case a suspension or a solution of the amide in xylene was treated with the carefully mixed finely ground phosphorus pentasulphide and potassium sulphide in amounts sufficient for the formation of potassium thiophosphate: $P_2S_5 + 3K_2S \rightarrow 2K_3PS_4$ (sometimes a slight excess of potassium sulphide is taken). This reaction goes especially well in pyridine[190].

In order to eliminate the inconvenience of working with a mixture of two solids (potassium sulphide and phosphorus pentasulphide), amides were treated with salts of thiophosphoric acid, this method giving yields of ~ 80% of thioacetamide[191,192]. An 80% yield of thioacetamide was also obtained by treating acetamide with a mixture of phosphorus pentasulphide and potassium sulphide (in the molar ratio: 1.5 : 5).[103]

The yield of thioamides depends on the nature of the initial amide. For example, treatment of acetamide in benzene with a mixture of phosphorus pentasulphide and potassium sulphide gave an 80% yield of thioacetamide, whereas the yield of isovaleramide was 0.4% (the main product being the nitrile).[103]

Thioamides can be obtained by the action of phosphorus pentasulphide on amides also in the absence of solvents[149,153-156,162-164]. In this case equimolecular quantities of the amide and phosphorus pentasulphide are melted together, and the thioamide is extracted from the resulting resinous mass with a suitable solvent. The yield of thioformamide prepared in this way is ~ 50%.[121]

The mechanism of the interaction of amides with phosphorus pentasulphide has not been established exactly. The reaction is presumably represented by the scheme[193]



6. PREPARATION OF THIOAMIDES BY REACTION WITH ALUMINIUM AND IRON SULPHIDES

Thioamides are formed by the action of aluminium sulphide on amides, nitriles, and ammonium salts[194-196], 1 or 2 moles of water being added to the mixture when an amide or a nitrile is used. This is usually added as water of crystallisation (e.g. $Na_2SO_4.6H_2O$). The process is conducted in a sealed tube or an autocalve at 200–250°C for ~ 90 min. When ammonium salts are used, water is not required.

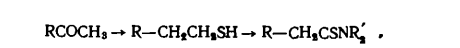
Aromatic and aliphatic thioamides are obtained in good yields by this method[194].

Sulphides of other metals, e.g. iron, can be used instead of aluminium sulphide[195].

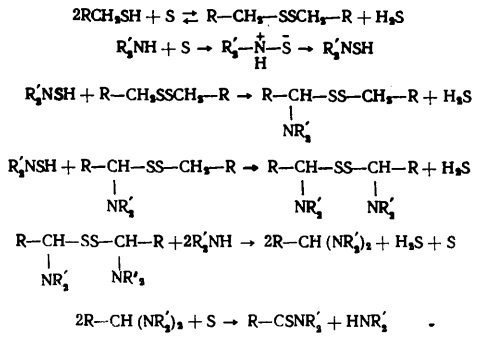
7. PREPARATION OF THIOAMIDES BY THE WILLGERODT–KINDLER REACTION

There exist several modifications of this method for obtaining thioamides—(*a*) reaction of sulphur with ketones or aldehydes in the presence of an equimolecular quantity of an amine[165,197-200], (*b*) direct oxidation of the amine by sulphur[201,202], and (*c*) interaction of sulphur with an alkyne and ammonia[203,206]—these three variants being included under the combined term the Willgerodt–Kindler reaction[207-227].

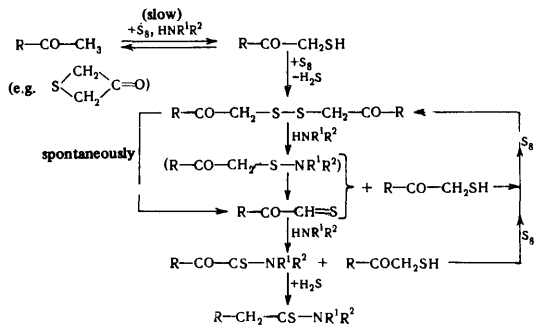
Several reviews have been devoted to this reaction[207-209,228,229], and special papers have been published on its mechanism[209,230-232]. However, the mechanism of the Willgerodt reaction is still not clear. Thiols are probably formed as intermediates, and are converted into thioamides[228]:



The conversion of thiols into thioamides takes place when both sulphur and an amine are present. The formation of thioamides is represented by the scheme



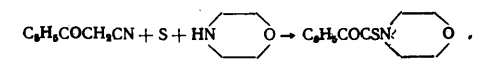
A rather different assessment of the mechanism of the Willgerodt–Kindler reaction has recently been expressed[224] in connection with an investigation of the formation of a thioamide from 3-oxothietan, a secondary amine, and sulphur:



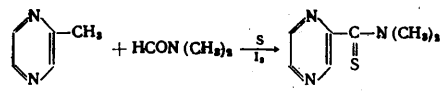
where R = CH_3. According to this scheme the reaction begins with formation of an α-mercapto-ketone, this being the rate-determining stage. The disulphide, which is formed very readily, passes via the oxosulphenamide into an oxo-thial. In the presence of an amine the oxo-thial undergoes disproportionation by the Cannizzaro reaction with formation of the α-mercapto-ketone and an α-oxo-thioamide, the latter then being reduced to the required thioamide.

There are also other interpretations of the mechanism of the Willgerodt–Kindler reaction. In this connection the view of several authors[165,182] must be accepted, that this reaction, which is characterised by a great variety of starting materials and process conditions, does not fit into a single mechanism.

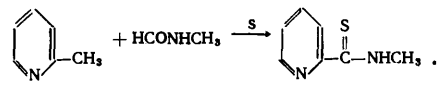
NN-Disubstituted thioamides can be obtained in good yield from aromatic aldehydes[212]. Under the conditions of this reaction diketones are reduced to monoketones, which then give thioamides[215]. α-Cyano-ketones form α-oxo-thioamides with loss of one carbon atom[216]:



Variants of the Willgerodt–Kindler reaction have been described in which certain heterocyclic compounds, dimethylformamide, and iodine are involved in the reaction[209,217,218]. Thus the *NN*-dimethylthioamide of pyrazine has been obtained from methylpyrazine, dimethylformamide, and sulphur in the presence of iodine[219]:

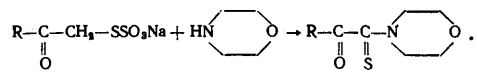


while the use of 2-methylpyridine and methylformamide yields *N'*-methylpyridine-2-thioamide[220]:



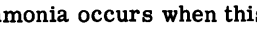
In this way quinaldine is converted into quinoline-2-thioamide. The reaction does not take place when anthranilic acid, *o*-aminophenol, sulphanilic acid, 2-aminothiazole, 2-amino-1,3,4-thiadiazole, or 2-aminopyridine is used as the amine component[221].

S-Acylmethyl thiosulphates form with amines good yields of *NN*-disubstituted α-oxo-thioamides[233,234]:

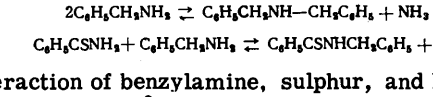


It has since proved possible to bring into reaction with sulphur secondary and tertiary alcohols, thiols, disulphides, imines, alkenes[206], diazo-ketones[200], Schiff bases[210], and also $\alpha\beta$-unsaturated acids[232] (in the last case thioamides are obtained having one carbon atom less than in the initial acid)[235–242].

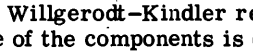
Thioamides are formed when amines are heated with sulphur even in the absence of carbonyl compounds[210,243–253]. Heating benzylamine with sulphur in a sealed tube at 180°C gives a 91% yield of thiobenzamide:



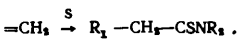
Copious evolution of ammonia occurs when this reaction is conducted in an open vessel[207]:



The interaction of benzylamine, sulphur, and lead monoxide in benzene at 20°C gives bisthiobenzamido-disulphide:



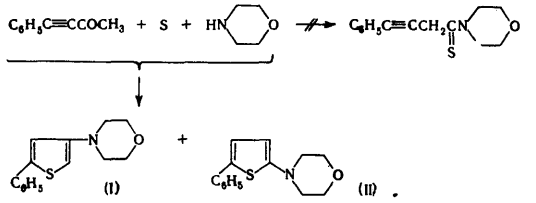
A modification of the Willgerodt–Kindler reaction in which an enamine is one of the components is of practical interest, the process being conducted in a polar solvent at room temperature. Thioamides in yields of ~ 75% are formed[222,223]:



Thioamides are formed by the action of sulphur on unsaturated hydrocarbons in the presence of ammonia or an amine. The reactions are conducted in dry solvents at 50–300°C, gaseous ammonia or a low-boiling amine (e.g. methylamine) being used under pressure. In this way the interaction of acetylene, sulphur, and ammonia (or an amine) in dioxan or pyridine at 50–100°C has been applied to the preparation of thioacetamide[249], dithio-oxamides, and other thioamides[203,204,250–253].

The interaction of styrene and sulphur in the presence of morpholine gives a 52% yield of phenylthioacetomorpholide[190], whereas in the presence of benzylamine the main product is phenylacetic acid contaminated by *N*-benzylthiobenzamide. Phenylthioacetomorpholide is obtained in 20% yield also by the action of sulphur on phenylacetylene and morpholine[232,254].

It has recently been shown that acetylenic ketones do not yield thioamides—as has hitherto been supposed—but isomeric thiophen derivatives[211]:



The ratio of the isomers (I) and (II) thus obtained is 9 : 1.

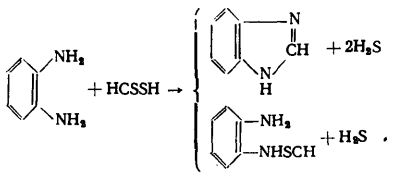
8. PREPARATION OF THIOAMIDES BY THE THIOACYLATION OF AMINES

The thioacylation—analogous to acylation—of amines often results in the formation of thioamides in very good yields. Carbodithioic acids[255-257], their salts[258-264], esters, and chlorides, as well as *O*-esters of carbothionic acids[261 265-268], are used as thioacylating agents. Depending on the reagent used, hydrogen sulphide, thiols, hydrogen chloride, and alcohols are also isolated in this reaction. The amines used are ammonia and primary and secondary amines.

An example of thioacylation by means of thiocarbonyl chlorides is the reaction of thiobenzoyl chloride with aniline to form thiobenzanilide[269]. This method is of no practical value because of the relative inaccessibility of thiocarbonyl chlorides[270]. Carbodithioic acids and their salts are used considerably more often‡. For example, sodium cyanodithioformate, obtained from carbon disulphide and sodium cyanide, gives with diethylamine and dimethylamine the *NN*-dialkylamides of cyanothioformic acid[273].

Potassium dithioformate‡ reacts with an aqueous solution of an amine at room temperature to form an *N*-substituted thioformamide; with water-insoluble amines the reaction is conducted in organic solvents (ether, chloroform, dioxan[262,274]). The yield of thioformamide obtained by the action of ammonia on dithioformic acid reached 30%, higher than in its preparation from formamide and phosphorus pentasulphide[262]. Aniline and 6-aminoquinoline give the corresponding substituted thioformamides in theoretical yields. The reaction does not take place with indole, diphenylamine, or *N*-methylaniline[262].

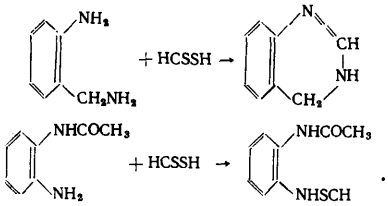
Diamines form with carbothioic acids unstable compounds, which readily undergo cyclisation. Thus *o*-phenylenediamine in aqueous solution at 10°C gives an unstable product, which at room temperature is rapidly converted into benzimidazole[262], though other results indicate that *N*-*o*-aminophenylthioformamide is produced in this case[271,272]:



‡The preparation of the initial carbodithioic acids and their derivatives has been studied in very great detail[228, 229,271,272].

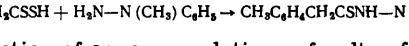
Cyclisation does not occur when dithioformic acids act on 4,5-diamino-6-methylpyrimidine[262] or on 4-amino-5-aminomethyl-2-methylpyrimidine[275-277], because of the feebly basic character of the amino-groups in the starting materials.

o-Aminobenzylamine and *o*-aminoacetanilide with dithioformic acid give quantitative yields of dihydrobenzopyrimidine and stable *N*-*o*-thioformamidoacetanilide[262]:

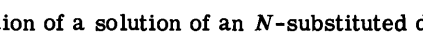


5-Thioacylpyrimidines, which are not formed from 5-acylpyrimidines and phosphorus pentasulphide, are easily obtained by this method[262,274-291].

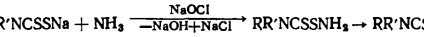
m-Tolyldithioacetic acid forms with 1-methyl-1-phenylhydrazine the corresponding hydrazide[292]:



By the action of aqueous solutions of salts of dithioacids on amines in the presence of an aqueous solution of iodine and potassium iodide *N*-substituted thioamides are formed in yields of 95–100%.[258,293] It is supposed that thioacylsulphenamides are formed initially, and split off sulphur to give the thioamides:



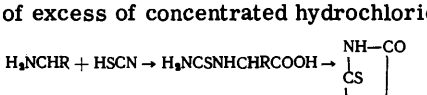
Thus addition of a solution of an *N*-substituted dithiocarbamate and iodine or 10% sodium hypochlorite solution (in equimolecular quantities) to excess of concentrated ammonia produces an *NN*-dialkylthioacylsulphenamide, which on prolonged standing or on heating passes into an *N*-substituted thiourea[294]:



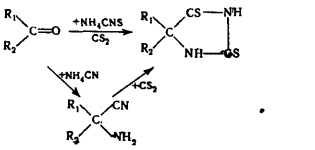
N-Chloropiperidine gives with salts of dithio-acids a quantitative yield of *N*-2′-thiofuroylpiperidine and *N*-thiobenzoylpiperidine. Here, too, sulphenamides are probably formed as intermediates[258,295].

Carbodithioic esters[255,256,296] are often used for the thioacylation of amino-acids[229,255,297-299]§ and the synthesis of purine derivatives[286], vitamin B_1,[274] and other biologically active substances. Equimolecular quantities of carboxymethyl dithiobenzoate and aminoacetic acid interact in

§Amino-acids are thioacylated also by the action of ammonium or potassium thiocyanate in acetic anhydride at 60–80°C, 1-acetyl-2-thiohydantoins being formed, from which the free 2-thiohydantoins can be isolated by the action of excess of concentrated hydrochloric acid[300]:



where R = H or CH_3. Ammonium thiocyanate acts on ketones in carbon disulphide to form dithiohydantoins[301,302]:



an aqueous solution of a base at room temperature to give a 90% yield of thiobenzoylglycine[299]:

$$C_6H_5CSSCH_2COOH + H_2NCH_2COOH \rightarrow C_6H_5CSNHCH_2COOH .$$

Similarly, the interaction of carboxymethyl dithiobenzoate and anthranilic acid gives a good yield of thiobenzoylanthranilic acid[299].

DL-Lysine interacts with carboxymethyl phenyldithioacetate to give a monoacylated derivative, probably $C_6H_5CH_2CSNH[CH_2]_4CH(NH_2)COOH$ (the product gives a positive ninhydrin reaction¶). No racemisation was observed in the thiobenzoylation of the L-stereoisomers of alanine, valine, isoleucine, and leucine[256]. Diethyl aminomalonate is more conveniently thiobenzoylated in pyridine to which triethylamine has been added[297]. The thiobenzylation of diamines gives good yields of polymethylenebisthiobenzamides $C_6H_5CSNH[CH_2]_xNHCSC_6H_5$ (x = 1–6). An α-aminoisobutyrate does not undergo thiobenzoylation, probably owing to steric hindrance[255,256].

Carboxymethyl dithioacetate as thioacylating agent is added in excess (10%) to a solution of the sodium salt of the amino-acid in alcohol[303-305]. N-2-Arylethylthioamides $RCSNHCH_2CH_2C_6H_5$ have been obtained by this method in yields of 86–99%.[306]

Thiobenzamides are formed in good yields by the reaction of dithioic esters with morpholine and with aniline[256]. Carbothionic esters RCSOR′ react similarly with amines[256,307,308]. In this way a phenylthiohydrazide has been obtained from phenylhydrazine and a carbothionic ester[263], the reaction being conducted in ether or excess of phenylhydrazine. The interaction of ethyl thiobenzoate with excess of 2-aminoethanol and isopropylamine respectively has given N-2-hydroxyethylthiobenzamide and N-isopropylthiobenzamide in yields of 53% and 63%.[261]

Good thioacylation results have been obtained by the interaction of carbothionic esters with substituted anilinomagnesium bromides[309,310]:

$$RO{-}C_6H_4{-}CS{-}OC_2H_5 + BrMgNHC_6H_4OR' \rightarrow RO{-}C_6H_4CS{-}NHC_6H_4OR' + C_2H_5OMgBr.$$

A convenient thioacylating reagent is a thioacylsuccimide, obtained in good yield by reaction of an aromatic unsubstituted thioamide with succinyl chloride[311]:

$$ArCSNH_2 + ClCOCH_2CH_2COCl \rightarrow ArCS{-}N\begin{matrix}CO{-}CH_2\\ |\\ CO{-}CH_2\end{matrix}$$

Unsubstituted thioamides are also thioacylating agents. Under mild conditions they undergo transamidation with primary aliphatic amines to form N-alkylated thioamides. This has been termed the Wallach reaction[312]. Several derivatives of dithio-oxamide have been obtained in this way, the two unsubstituted thiocarbamoyl groups being involved in the reaction[313]:

$$2R{-}CH_2{-}NH_2 + H_2N{-}CS{-}CS{-}NH_2 \rightarrow R{-}CH_2{-}NH{-}CS{-}CS{-}NH{-}CH_2{-}R + 2NH_3$$

where R = COOH, SO_3H. Only the thiocarbamoyl group is involved in the reaction of monothio-oxamide with aliphatic amines[143,312]. Morpholine reacts with dithio-oxamide to give N-morpholinodithio-oxamide[44,313], and other thio-oxamides have recently been obtained by this method[314]. Amino-acids also can be thioacylated with dithio-oxamide[315]. NN-Dimethylthioformamide gives amidines with amines[316].

Substituted thioformamides are obtained in good yield by the interaction of chloroform, an amine, and hydrogen sulphide in alkaline solution[317]. It is assumed that dichlorocarbene is formed initially from the chloroform (by α-elimination), and then reacts according to the equation

$$:CCl_2 + R'R''NH + 2SH^- \rightarrow R'R''N{-}CSH + H_2S + 2Cl^- .$$

9. PREPARATION OF THIOAMIDES BY THE REACTION OF ISOTHIOCYANATES WITH ORGANOMETALLIC COMPOUNDS, C–H ACIDS, AND ENAMINES

These reactions are employed considerably more rarely than those considered earlier for the preparation of thioamides. They are based on the addition of nucleophilic reagents at the multiple bond in an isothiocyanate, and in this respect show great similarity to the corresponding reactions of isocyanates:

$$R{-}\overset{\delta+}{N}{=}\overset{\delta-}{C}{=}\overset{\delta-}{S} + R'{-}\overset{\delta+}{X} \rightarrow R{-}N{=}\underset{R'}{\overset{|}{C}}{-}SX \xrightarrow[-OHX]{H_2O} R{-}NHC{=}\underset{R'}{\overset{|}{S}}$$

where X = M, H. The symbol X denotes a metal when an organometallic compound[318-333] or a C–H acid in the form of its sodium or lithium salt is used, and hydrogen in the case of an enamine.

The reaction between isothiocyanates and organometallic compounds was first studied by the use of Grignard reagents. Thioamides are obtained in good yield by the action of Grignard reagents on phenyl isothiocyanate followed by hydrolysis of the addition products[258,318-320]:

$$C_6H_5N{=}C{=}S + CH_3MgI \rightarrow C_6H_5N{=}C(CH_3){-}S{-}MgI \rightarrow C_6H_5NHCSCH_3 .$$

The action of dimethyl sulphate on the addition product of phenylmagnesium bromide and phenyl isothiocyanate gave an S-methyl derivative of an isothioamide[321]:

$$C_6H_5{-}N{=}C(C_6H_5){-}S{-}MgBr + (CH_3O)_2SO_2 \rightarrow C_6H_5N{=}C(C_6H_5)SCH_3 .$$

N-Substituted thioamides of valeric acid were obtained in 90% yield by the reaction of n-butylmagnesium bromide with isothiocyanates[322]. Phenylmagnesium bromide reacts with phenyl isothiocyanate to give thiobenzamide in 88% yield[288].

Isothiocyanates react with excess of a Grignard reagent at high temperatures to give other products. Thus a 45% yield of o-phenyldiphenylmethylaniline was obtained from phenyl isothiocyanate and phenylmagnesium bromide[323].

Bifunctional thioamides are formed by the interaction of sodium alkyls with phenyl isothiocyanate[325-328]:

$$\overset{\delta-\ \delta+}{RCH_2Na} + C_6H_5N{=}\overset{\delta+\ \delta-}{C{=}S} \rightarrow RCH_2\underset{NC_6H_5}{\overset{||}{C}}SNa \xrightarrow[-H]{+Na}$$

$$\rightarrow \underset{Na}{\overset{\delta-}{RCH}}{-}\underset{NC_6H_5}{\overset{||}{C}}{-}SNa \xrightarrow{C_6H_5N=C=S} \underset{\quad C{-}SNa}{\overset{NC_6H_5}{\overset{||}{RCH}}} \xrightarrow[-2NaOH]{+2H_2O} \underset{\quad CSNHC_6H_5}{\overset{CSNHC_6H_5}{RCH}} .$$

$$\underset{\quad C{-}SNa}{\overset{NC_6H_5}{\overset{||}{RCH}}}$$

1,2-Addition products of sodium to alkenes react with isothiocyanates to form disodium derivatives, which can be hydrolysed to bisthioamides[327,334]:

$$2C_2H_5NCS + (C_6H_5)_2CNa{-}CNa(C_6H_5)_2 \rightarrow C_2H_5N(Na)CSCSN(Na)C_2H_5 + (C_6H_5)_2C{=}C(C_6H_5)_2$$

$$2C_2H_5NCS + (C_6H_5)_2CNaCH_2CH_2CNa(C_6H_5)_2 \rightarrow (C_6H_5)_2{=}\underset{CSN(Na)C_2H_5}{\overset{|}{C}}{-}CH_2CH_2(C_6H_5)CSN(Na)C_2H_5 .$$

¶ Boiling amino-acids with an aqueous solution of ninhydrin (indane-1,2,3-trione hydrate) produces a blue coloration.

Organolithium compounds also can be used as the organometallic compounds. Thus 3-methyl-2,2-diphenylbut-3-enothioanilide was isolated after reaction with phenyl isothiocyanate of the organolithium compound obtained from the corresponding alkene and lithium[327], a 57% yield of thiobenzamide after reaction with triphenylsilyl isothiocyanate[329], and *N*-phenylthiobenzamide when phenyl isothiocyanate was used [with phenyl-lithium][330]:

$$C_6H_5Li + C_6H_5NCS \rightarrow C_6H_5N(Li)CSC_6H_5 \xrightarrow{H_2O} C_6H_5NHCSC_6H_5 + LiOH .$$

Triethylaluminium (or a mixture of ethylaluminium dichloride and diethylaluminium chloride) gives with aliphatic and aromatic isothiocyanates a series of thioamides of propionic acid in yields of 58–96%.[331,332]

Phenyl isothiocyanate reacts with sodium tetrahydroborate to form thioformanilide[333,335]:

$$C_6H_5N{=}C{=}S + NaBH_4 \rightarrow [C_6H_5{-}NHCS{-}BH_3Na] \xrightarrow{H^+} C_6H_5NH{-}\underset{\underset{S}{\|}}{C}{-}H .$$

Isothiocyanates react with C–H acids in practically the same way as with organomagnesium compounds, since these acids are usually employed in the form of their alkali-metal salts[324,336–350]:

$$R'{-}\underset{R''}{\overset{R}{C}}{-}Na + R'''NCS \rightarrow R'{-}\underset{R'}{\overset{R}{C}}{-}\underset{\underset{S}{\|}}{C}{-}N(R'''){-}Na \xrightarrow[-NaCl]{+HCl} R'{-}\underset{R'}{\overset{R}{C}}{-}\underset{\underset{S}{\|}}{C}{-}NR''H .$$

Triphenylmethylsodium reacts with isothiocyanates, e.g. with allyl isothiocyanate to form *N*-allyltriphenylthioacetamide[328].

Sodiomalonic ester gives with *p*-phenylene di-isothiocyanate in absolute alcohol the sodium salts of mono- and di-addition products, from which acidification yields diethyl *N*-*p*-isothiocyanatophenylthiocarbamoylmalonate (*a*) and tetraethyl *p*-phenylene-*NN'*-bisthiocarbamoylmalonate (*b*):[348]

$$S{=}C{=}N{-}C_6H_4{-}NH{-}CS{-}CH(COOC_2H_5)_2 \quad (a)$$

$$(C_2H_5OCO)_2CH{-}CS{-}NHC_6H_4NH{-}CS{-}CH(COOC_2H_5)_2 . \quad (b)$$

Sodioacetoacetic ester forms only the monoaddition product, which breaks down in alcoholic solution at room temperature into ethyl acetate and ethyl *N*-*p*-isothiocyanatophenylthiocarbamoylacetate[349,350]:

$$S{=}C{=}N{-}C_6H_4NHCS{-}\underset{COOC_2H_5}{\overset{COCH_3}{C}}{-}H \rightarrow S{=}C{=}N{-}C_6H_4NHCS{-}CH_2COOC_2H_5 + CH_3COOC_2H_5 .$$

Sodium acetylacetonate reacts with aryl isothiocyanates in absolute alcohol to form *NN'*-diarylated bisthioamides of malonic acid[349].

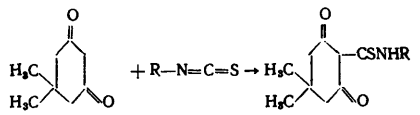
The sodium salt of acetylthioacetanilide reacts with phenyl isothiocyanate to give the dianilide of acetylmalonodithionic acid[350]:

$$CH_3{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{Na}{|}}{CH}{-}\underset{\underset{S}{\|}}{C}{-}NHC_6H_5 + C_6H_5N{=}C{=}S \rightarrow CH_3{-}\underset{\underset{O}{\|}}{C}{-}\underset{CSNHC_6H_5}{\overset{CSNHC_6H_5}{C}}{-}H .$$

Other derivatives of malonodithionic acid have been obtained by using substituted phenyl isothiocyanates under the same conditions.

Cyclic C–H acids also react with isothiocyanates to form thioamides. In this way good yields of variously substituted anilides of pyrrolecarbothionic acid have been obtained by the use of pyrrole[351].

The addition of isothiocyanates to dimedone in acetonitrile in the presence of a small amount of alkali[352] leads to the formation of a thioamide in 60% yield:

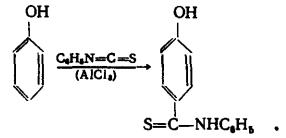


where R = C_6H_5, *p*-ClC_6H_4, *p*-$NO_2C_6H_4$, 1-naphthyl. The reaction does not take place in ethanol[353].

Alkali-metal cyanides give with isothiocyanates *N*-substituted cyanothioformamides, which react with hydrogen sulphide to produce *N*-substituted dithio-oxamides[354]. The best yields of thioamides are obtained with potassium cyanide:

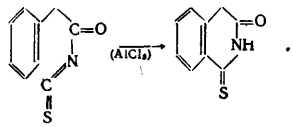
$$KCN + R{-}NHCS \rightarrow R{-}NHCSCN \xrightarrow{H_2S} R{-}NH{-}CS{-}CS{-}NH_2 .$$

Alkoxyphenyl isothiocyanates form with sodium cyanide alkoxylated cyanothioformamides, which are converted by hydrogen sulphide into alkoxyphenyldithio-oxanides[355]. Isothiocyanates react with phenols in the presence of aluminium chloride[356–359], with the formation not of thioneurethanes but of thioamides:



Thioamides are formed with phenyl ethers (and also ethyl phenyl sulphide) and phenyl isothiocyanate[360].

In the presence of aluminium chloride phenylacetyl isothiocyanate undergoes intramolecular rearrangement to give a 40–70% yield of homomonothiophthalamide[361]:

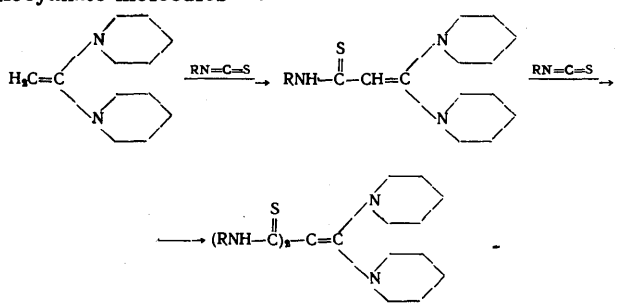


Isothiocyanates react in the presence of aluminium chloride also with aromatic hydrocarbons[362].

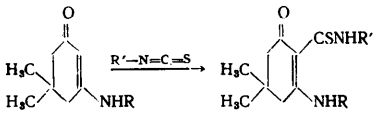
Enamines react with aryl isothiocyanates to form amides of β-aminocycloalkenecarbothioic acids, which are readily saponified to thioamides of β-oxo-carboxylic acids[363–365]:

$$H{-}C{=}C{-}NR_2''' \xrightarrow{R''''{-}N{=}C{=}S} R''''{-}NH{-}\underset{\underset{S}{\|}}{C}{-}\underset{R'}{\overset{R''}{C}}{-}NR_2''' .$$

The enamine of 1,1-dipiperid-1'-ylethylene adds two isothiocyanate molecules[366]:

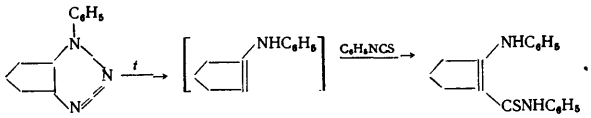


where R = Ar, Alk. Cyclic enamines also react with isothiocyanates[352]:



where R = H, CH_3 and R′ = C_6H_5, p-ClC_6H_4, p-$NO_2C_6H_4$.

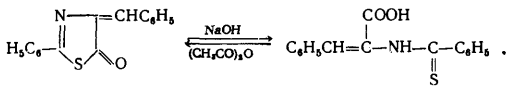
Substituted Δ^1-triazoles react with isothiocyanates to form thioamides (yield 50–99%):[367–370]



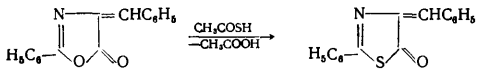
10. PREPARATION OF THIOAMIDES BY THE CLEAVAGE OF HETEROCYCLES

Certain heterocyclic compounds (derivatives of thiazole and oxazole) can undergo cleavage under the influence of alkaline reagents or hydrogen sulphide, thioamides being formed[371–374].

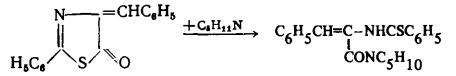
When 4-benzylidene-2-phenylthiazol-5-one is boiled with dilute caustic soda, α-thiobenzamidocinnamic acid $C_6H_5CH{:}C(NHCSC_6H_5)COOH$ is formed[371]. This reaction is reversible, heating the resulting substituted cinnamic acid with acetic anhydride giving an 85% yield of the original thiazolone[371]:



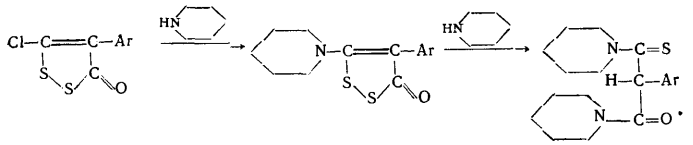
The original 4-benzylidene-2-phenylthiazol-5-one was prepared by the reaction of 4-benzylidene-2-phenyloxazol-5-one with thioacetic acid[371]:



Heating this thiazolone with piperidine gives an N-piperidyl derivative of α-thiobenzamidocinnamic acid in 60% yield:

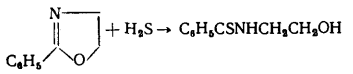


Mixed thioamide–amides of arylmalonic acids are obtained by the action of amines on 4-aryl-3-chloro-5-keto-1,2-dithioles[373]:

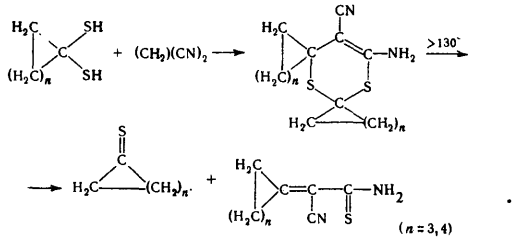


Similarly, N-α-thiobenzamidodihydrocinnamoylpiperidine is obtained from 4-benzyl-2-phenylthiazolone.

Thioamides are formed also by the cleavage of oxazolines by hydrogen sulphide. Treatment of a solution of 2-phenyloxazoline in methanol with ammonium sulphide (or ammonium hydroxide and hydrogen sulphide) gave N-2-hydroxyethylthiobenzamide (yield 77%):[261]

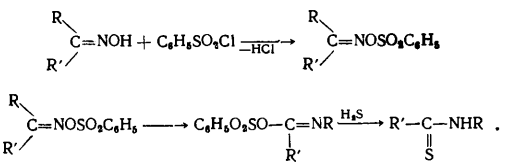


Substituted 1,3-dithi-ins, formed from *gem*-dithiols and malononitrile, when heated decompose into thioketones and thioamides[374]:



11. CONVERSION OF BENZENESULPHONATES OF KETOOXIMES INTO THIOAMIDES

Benzenesulphonates of ketoximes, formed by the action of benzenesulphonyl chloride on the ketoximes in pyridine, are converted in the presence of hydrogen sulphide, as a result of spontaneous Beckmann rearrangement into sulphonimidates, into good yields of N-substituted thioamides[375–378]:



A great variety of thioamides have been obtained by this method using aliphatic, cyclic, aromatic, and mixed ketoximes.

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Chemical Properties of 1,3-Dioxans

I.Apok, M.Bartok, R.A.Karakhanov, and N.I.Shuikin

A detailed description is given of the chemical properties of 1,3-dioxans. Special attention is paid to their thermal and catalytic reactions, and also to the preparation from them of various 1,3-bifunctional aliphatic compounds. Detailed consideration is given to the hydrolysis and the alcoholysis of dioxans, and their interaction with derivatives of carboxylic acids and also with certain inorganic compounds containing labile halogen atoms, etc. The mechanism of the various reactions of 1,3-dioxans are surveyed and discussed in detail on the basis of numerous examples. The bibliography contains 155 references.

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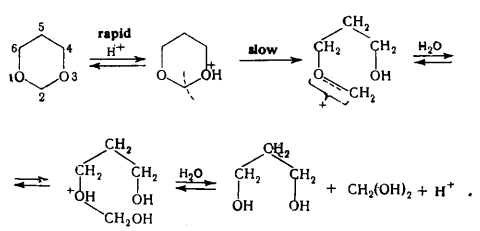
I. INTRODUCTION

The widespread application of the Prins reaction[1] has enabled alkenes[2], obtained in the petroleum-chemical industry, to be used for the single-stage synthesis of several valuable products—1,3-dioxans, diols, unsaturated alcohols, etc.—which can be employed directly as solvents, antiknock compounds, or as intermediates for the synthesis of medicinal preparations, plastics, etc. Publication of a review[2] was followed by considerable progress in the synthesis of 1,3-dioxans, connected in great measure with the use of solid electrophilic catalysts such as mineral acids on carriers (natural and synthetic aluminosilicates) and ion-exchange resins. The use of solid catalysts and flow-type apparatus in particular permitted a considerable simplification in the technology and improvement in the efficiency of the manufacture of 1,3-dioxans. The great quantity of new data which have been published on the transformations undergone by 1,3-dioxans are undoubtedly worthy of special discussion.

Most of the papers and patents which have been published recently have been concerned with the thermal and catalytic cracking of dioxans, and also their conversion into 1,3-bifunctional aliphatic compounds. Special attention will be paid to this question in the present review.

II. HYDROLYSIS OF 1,3-DIOXANS

The vapour-phase catalytic cracking of dioxans in the presence of water vapour involves chemical processes yielding products whose formation can be explained by hydrolysis of the dioxans and accompanying secondary reactions. Like the hydrolysis of acetals[3,4], that of 1,3-dioxans[5-13] is a second-order unimolecular reaction, since its rate is determined by the rate of formation of a carbon cation[12], the reaction being represented by the scheme:



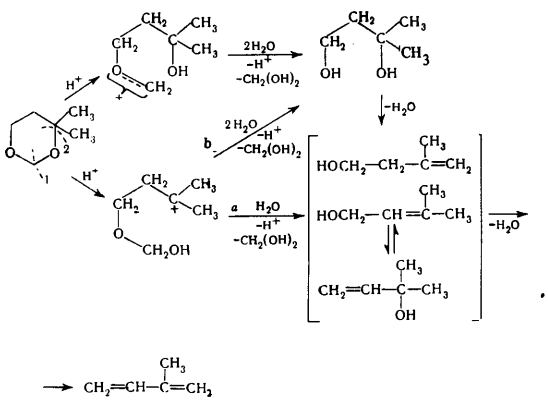
The first stage in the reaction involves addition of a proton, and is followed by slow cleavage of the 1,2- or 2,3-carbon–oxygen bond with formation of a carbon cation, which reacts with two water molecules to give an oxo-compound and a diol.

The above scheme shows that the hydrolysis of 1,3-dioxans in the presence of acid catalysts yields mainly the corresponding 1,3-diols, derivatives thereof[2,5-21], and oxo-compounds. The yield of diols varies within wide limits, since the reaction is reversible, and also because the diols undergo partial dehydration under the conditions of hydrolysis. The equilibrium can be shifted towards the diols by adding alkenes to the reaction mixture[2,14], when the formaldehyde resulting from hydrolysis reacts with the alkene to form the initial dioxan. The yield of 1,3-diol is considerably increased.

Depending on the structure of the 1,3-dioxans, under certain conditions hydrolysis leads directly to formation of conjugated 1,3-dienes[22-26]. This process occurs especially easily with 4,4-dialkyl-1,3-dioxans, hydrolysis of which involves rupture of the 3,4-carbon–oxygen bond as well as the usual cleavage of the 1,2- or 2,3-bond.

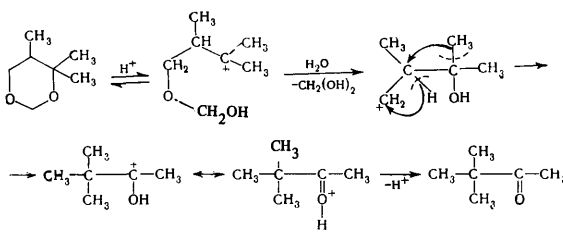
Stabilisation of the tertiary carbon cation which is formed[18,27], ultimately yielding a conjugated diene, can probably be achieved in two ways—(*a*) by loss of a proton

and formation of an unsaturated alcohol, and (*b*) by addition of two molecules of water with formation of a tertiary diol:



Alcoholysis of 4,4-dimethyl-1,3-dioxan gave a 30% yield of the corresponding tertiary ether[20,28,29], whose formation can be explained by interaction of the corresponding carbonium ion with the alcohol.

Many workers have studied the hydrolysis of polyalkylated dioxans. Thus a 50% yield of pinacoline was obtained by treating 4,4,5-trimethyl-1,3-dioxan with a 20% solution of hot hydrochloric acid[26,30], but the reaction mechanism was not discussed. The reaction can probably be represented by a double 1,2-type of rearrangement with migration of a hydride anion in the first stage and of a carbanion in the second stage:



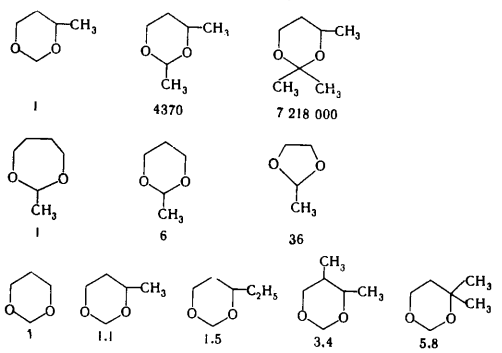
The action of dilute mineral acids (hydrochloric, sulphuric) on 4,4,5-trimethyl-1,3-dioxan gives a 50% yield of 2,3-dimethylbuta-1,3-diene[22,25,26]. The hydrolysis of 1,3-dioxans obtained from polyols leads to the formation of 1,3-dioxolans, which are in equilibrium with the initial dioxans[31]. Phenyldihydropyran has been obtained[32] by hydrolysis of 4-2'-hydroxyethyl-4-phenyl-1,3-dioxan and dehydrocyclisation of the resulting unsaturated diol.

Ion-exchange resins (Amberlite IR-120, Dowex 50-WX-4) are good catalysts for the hydrolysis of 1,3-dioxans[15,33]. Thus the latter have been used to effect the partial hydrolysis of the acetal of pentaerythritol[15]. A patent reports use of the boron trifluoride–ether complex for the hydrolysis of 4,4-dimethyl-1,3-dioxan, when isoprene was obtained as a result of hydrolysis and dehydration[24].

Skrabal[5] and Leutner[6,7] studied the kinetics of the hydrolysis of cyclic acetals in the presence of hydrochloric acid at room temperature. To obtain comparative data they examined the hydrolysis of cyclic acetals containing five-, six-, and seven-membered rings. Table 1, which we have compiled from the work of Leutner and of Gershkovich[18], enables us to compare the stability of various cyclic acetals and ketals under conditions of acid hydrolysis and to reach certain conclusions. Table 1 shows that increase in the number of alkyl radicals in position 2 of the dioxan ring produces a sharp increase in the rate of hydrolysis of the 1,3-dioxans, which enables us to trace the rule in the sequence formal–acetal–ketal (first series).

The authors showed also that the rate of hydrolysis of cyclic acetals increases as the ring becomes smaller (second series). Alkyl radicals in position 4 of the ring have a considerably smaller effect on the rate of hydrolysis (third series). The effect of aryl radicals in position 2 of the 1,3-dioxan ring was studied by Ceder[8], who showed that the rate of hydrolysis of 2-substituted 1,3-dioxans increases in the sequence—2-methyl < 2,2-diphenyl < 2-phenyl < 2-methyl-2-phenyl < 2,2-dimethyl < 2-β-styryl.

Table 1.



* The numerals below the formulae denote relative rates of hydrolysis in the given series.

Thus electron-donor substituents in position 2 increase the rate of hydrolysis of 1,3-dioxans by facilitating the formation of a carbonium ion.

Bender and Silver[10] have studied the effect of substituents in a 2-phenyl ring on the rate of hydrolysis of dioxans. They have shown that hydrolysis is accelerated by *ortho*- and *para*-hydroxyls. It is possible that direct intramolecular action of the hydroxyl on the dioxan ring takes place in the case of 2-*o*-hydroxyphenyl-1,3-dioxan. However, a high rate of hydrolysis is found also with 2-*p*-hydroxyphenyl-1,3-dioxan, where intramolecular interaction of this kind is impossible. In general these facts can obviously be explained by the strong electron-donor effect of the phenoxide ion formed under the experimental conditions[10].

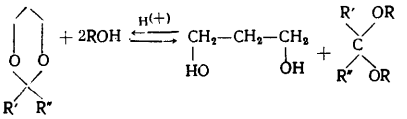
The kinetics and the mechanism of the hydrolysis of 1,3-dioxans have been discussed by Laurent et al.[9] and also by Aftalion et al.[11-13] on the basis of a large amount of experimental data. From their results they calculated several thermodynamic constants—enthalpy, activation energy, etc.—and found the hydrolysis to be endothermic, with an activation energy of approximately 26 cal mole^{-1}.

1,3-Dioxans containing electron-acceptor substituents in position 2, obtained from diols and chloral, are extremely resistant to hydrolysis, since the electron-acceptor groups prevent formation of a carbonium ion[17]. In some cases hydrolysis of the dioxans can be catalysed by traces of carbon dioxide[7]. Thus 5,5-dimethyl-1,3-dioxan-2-spirocyclopentane in an aqueous medium containing a mere trace of carbon dioxide gives 2,2-dimethylpropanediol and cyclopentanone. However, this course of reaction was not observed with the ketals of cyclohexanone and acetone.

The difference in behaviour between the dioxans was explained[33] by internal strain. Transition of a carbon atom from the tetracovalent state (ketal) to the trigonal state (cyclic ketone) is energetically more favourable in the case of cyclopentanone than with cyclohexanone[34]. The same reasons can obviously explain the hydrolysis of the acetals of 2,2-dimethylpropane-1,3-diol when they are boiled in 1,4-dioxan solution even in the absence of traces of mineral acids[15].

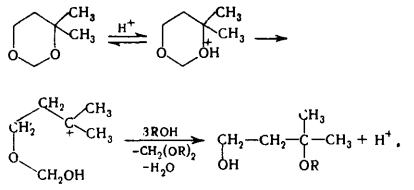
III. ALCOHOLYSIS OF 1,3-DIOXANS

1,3-Diols are obtained in good yield by the reaction between 1,3-dioxans and alcohols in the presence of acidic and electrophilic catalysts[2,27,29,35-41]:

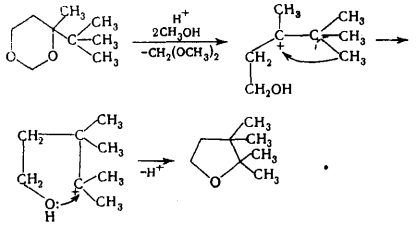


where R′, R″ = H, Alk and R = Alk. Acetals formed at the same time as the diols can be distilled from the reaction mixture, which shifts the equilibrium completely towards formation of diols. The mechanism of this reaction is analogous to that of the hydrolysis of 1,3-dioxans in the presence of acids.

Under certain conditions the alcoholysis of dioxans containing a quaternary carbon atom may lead to the formation of dienes[29,42,43], accompanied by ethers of tertiary alcohols[20,28,29]. The reaction mechanism probably includes formation of a carbonium ion[18,27]:



Korotkov et al.[27] report the formation of tetrahydrofuran compounds by the alcoholysis of 1,3-dioxan derivatives. The reaction involves cleavage of a carbon–oxygen bond adjacent to a tertiary carbon atom, followed by a retropinacoline rearrangement, leading to formation of a tetrahydrofuran ring:

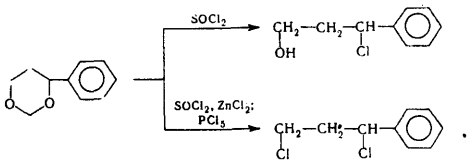


IV. INTERACTION OF 1,3-DIOXANS WITH INORGANIC COMPOUNDS CONTAINING LABILE HALOGEN ATOMS

Little work has been done on the reactions of 1,3-dioxans with inorganic halogen compounds. In 1912 the first study was made of the interaction of 1,3-dioxan with bromine, when a heavy oil, slowly decomposed by water, was formed[44]. The chlorination of 1,3-dioxans in the absence of moisture produced polychlorinated dioxans[2], whereas in aqueous solution 1,3-diols were formed in good yield.

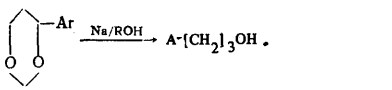
The chlorination of 4,4-dialkyl-1,3-dioxans in sodium carbonate solution produces 1,3-diols[45], one of the hydroxyls being attached to a tertiary carbon atom[46]. Compounds having this structure cannot be obtained by the hydrolysis of 1,3-dioxans, since under the conditions of the reaction the diols formed as intermediates are readily dehydrated to unsaturated alcohols and dienes.

In a large excess of thionyl chloride, as well as in the presence of concentrated hydrochloric acid, 3-phenyl-3-chloropropanol[46] is formed from 4-phenyl-1,3-dioxan, whereas in carbon tetrachloride a 50% yield of 1-phenyl-1,3-dichloropropane is obtained. Replacing the thionyl chloride by phosphorus pentachloride increases the yield to 95%:[46]

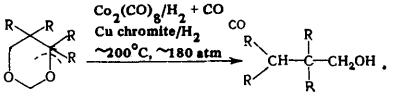


V. HYDROGENOLYSIS OF 1,3-DIOXANS

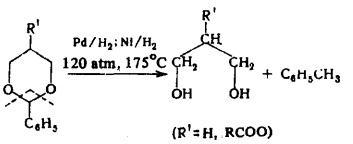
The hydrogenolysis of 1,3-dioxans leads to the formation of alcohols, the corresponding diols, or their monoethers depending on the conditions and the catalyst chosen and also on the structure of the initial compounds. This reaction has been widely studied by many investigators under various conditions in the presence of a large number of catalysts. Thus the hydrogenolysis of 1,3-dioxans has been investigated in the presence of metallic sodium in alcohol[32,47-53], Raney nickel[54,55], nickel[56], palladium[57-60], and platinum[61] catalysts, and also copper chromite[2,40,53,62-65] and octacarbonyldicobalt[66]. The changes undergone by 4-arylated dioxans have been investigated in the presence of metallic sodium and 2,6-dimethylheptan-4-ol, when the corresponding primary alcohols were obtained in yields exceeding 80%:[32,47-53]



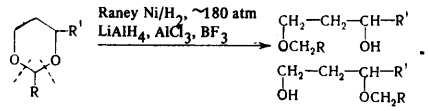
It was shown also that the hydrogenolysis of 1,3-dioxans containing mono- or poly-alkyl or -aryl substituents in positions 4 and 5 of the dioxan ring, on copper chromite or in the presence of octacarbonyldicobalt, leads to the formation of primary alcohols having an iso-structure[2,40,53,62-66]:



However, the use of metallic catalysts—nickel, palladium—for the hydrogenolysis of dioxans makes it possible to obtain 1,3-diols in good yield[56-60], whereas on platinum under analogous conditions the dioxan ring remains unchanged[61]:

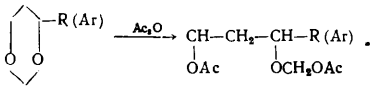


The hydrogenolysis of 1,3-dioxans in the presence of a Raney nickel–aluminium catalyst at high pressures leads to the formation of 1,3-alkoxyalkanols [54,55]. Similar results have been obtained with lithium tetrahydroaluminate and aluminium chloride, or the boron trifluoride–ether complex, as catalyst [67–70]:



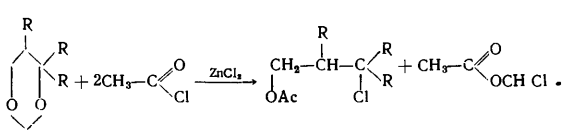
VI. REACTIONS OF 1,3-DIOXANS WITH DERIVATIVES OF CARBOXYLIC ACIDS

Many papers have been published on the reaction between 1,3-dioxans and acetic anhydride. This usually results in ester derivatives of a 1,3-diol in yields reaching 80%:[40,71–77]



Ness et al.[71] showed that, after the dioxan ring has been opened, the acetoxymethoxy-group adds to a secondary carbon atom. Results obtained by other workers[40,72–77] show that the dioxan ring is opened in only one way, whereas according to Shorygina[46,78] the esterification of 4-phenyl-1,3-dioxan may involve cleavage of the acetal ring at two bonds.

In the presence of electrophilic catalysts the chlorides of carboxylic acids open the dioxan ring to form 3-chloroacetoxyalkanes[79,80]:



These reactions are of industrial value, since the products can be used as plasticisers, solvents, etc.[79,80].

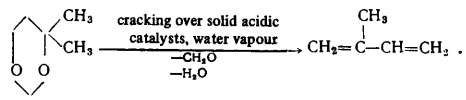
VII. THERMAL AND CONTACT–CATALYTIC REACTIONS OF 1,3-DIOXANS

Several scientific papers and patents have recently appeared on the thermal and catalytic transformations of 1,3-dioxans. These reactions of dioxans are not only of theoretical interest (in connection with the mechanism of the reaction, and the effect of the structure of 1,3-dioxans on the mechanism of catalysis) but also of great practical value. It has been found that good yields of extremely valuable conjugated dienes can be obtained by cracking 4- or 5-mono- or -di-alkyl-1,3-dioxans, synthesised by the Prins method from cheap industrial starting materials (alkenes and formaldehyde), over solid dehydration catalysts of acidic type[27,39,82–124]. The practical value of this reaction stimulated enhanced interest in the changes undergone by 1,3-dioxans, and led to the appearance of numerous publications and patents.

A systematic study of the conditions under which the process could be carried out and also the choice of catalysts was of primary importance for investigating the catalytic cracking of 1,3-dioxans. The pyrolysis of a cyclic acetal, 2-propyl-1,3-dioxan, was first reported by Bilger and Hibbert[81], who showed that, under the conditions of pyrolysis, cyclic acetals are more stable than the isomeric esters. These workers assumed that the reaction takes place by a radical mechanism.

Hamamoto and Mitsutani[122] investigated metal oxides and sulphates as catalysts. As the active component of the catalyst for the preparation of dienes from 1,3-dioxans many workers have used phosphoric acid, its acid salts, organic and inorganic phosphates on carriers and in their absence[27,39,82–112,114–124]. The carriers used have been graphite[82], coke[118], silica gel[84,90,104,114], silica–alumina[115,116], neutral silicates[101,105,108], kaolin[98], zeolite[114], kieselguhr[90,97,121], pumice[90], titanium dioxide[102,107–110], quartz[103,108–112], glass wool[105,108–110], aluminium oxide[84,90,114], silicon carbide[100,106,108–110], diatomite[99], and also mixed carriers[97].

An extremely interesting report has appeared on the transformation of 4,4-dimethyldioxan when passed together with triethyl phosphate through a tube containing silica gel heated to 400°C.[120] 4-Alkyl, 4,4-dialkyl-, and 4,5-polyalkyl-1,3-dioxans form dienes in yields which reach 90% depending on the reaction conditions[27,39,82–124]:



Water vapour is most often used as "diluent" in these processes, and plays an important part in maintaining the equilibrium of the acid phosphates in the catalytic decomposition of dioxans[94,115]. Nitrogen and the vapours of organic solvents are also employed as diluents[84,102,121]. The pyrolysis of 1,3-dioxans has been investigated over a wide range of temperatures of 150° to 450°C. The best results have been obtained at 200–350°C. There are indications that the relative proportion of side and secondary reactions increases as the period of contact becomes longer, the process shifting towards formation of isobutene or leading to the production of polymers of dienes and formaldehyde[94,117]. The pyrolysis of 1,3-dioxans has been investigated at atmospheric or nearly atmospheric pressures, but in several cases in which diluents were used the partial pressure of dioxan was 50–100 mmHg.

The effect of the nature of the catalyst and of the conditions of cracking has been investigated in detail for the conversion of 4,4-dimethyl-1,3-dioxan into isoprene[94,115,116,122,123]. The course of the reaction was shown to be greatly influenced by the nature of the carrier, its composition, and its structure, and also by the quantity of active component and the conditions under which the catalyst had been prepared (e.g. the temperature of ignition), as well as by the reaction temperature, the space velocity, etc.

In the cracking of 4,4-dimethyl-1,3-dioxan acidic carriers exhibit catalytic activity even in the absence of an active phase. In this case, however, the process exhibits poor selectivity towards formation of isoprene, the main product being isobutene[94,115]. Aluminium silicate, B_2O_3.Al_2O_3, Al_2O_3, SiO_2, $ZnO–SiO_2$, $Cr_2O_3.Al_2O_3$, and metal sulphates also catalyse the cracking of dimethyldioxan[94,113,115,122], the yield of isoprene being small.

A catalyst obtained by impregnating aluminium silicate with acid phosphates and then igniting possesses quite different properties. Both the yield and the selectivity are increased.

The properties of a catalyst depend substantially on the composition of the carrier. Thus increasing from 5% to 10% the alumina content of the carrier leads to a diminution in the selectivity and the stability of the catalyst[115].

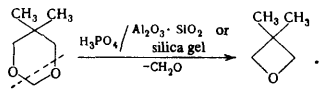
The explanation is that increase in the basicity of the carrier is accompanied by a change in the composition of the phosphate polymers formed on the catalyst surface during its ignition.

Another factor determining the activity and the selectivity of a catalyst is the concentration of active phase on the surface of the carrier and the associated proton acidity of the catalyst[116]. With increase in concentration of the active phase up to 4% a slow linear increase in proton acidity is observed; but with further increase in concentration the slope of the curve becomes greater. On the other hand, the activity and the selectivity of the catalyst with respect to isoprene increase rapidly over the section corresponding to saturation of the catalyst surface by phosphate polymers, i.e. up to 4–5% of the active phase; with further increase in concentration of the active phase and the associated acidity of the catalyst, the increase in activity and selectivity slows down, and constant values are reached[116].

1,3-Dioxans are regarded[116] as undergoing conversion both on Brønsted and on Lewis acid centres. However, the roles of the two types are different[115]. The formation of isoprene is attributed to the action of Brønsted acid centres, while the conversion of dioxan into isobutene and carbon is ascribed mainly to reaction on Lewis acid centres. Reversible adsorption of dioxans on the Brønsted centres is effected by oxygen atoms of basic character, and as a result intermediate ionic complexes are formed on the surface. These complexes break down to form dienes.

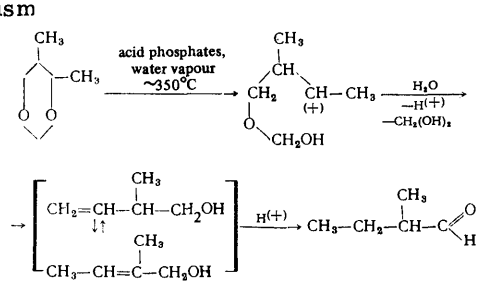
Cleavage of a carbon–carbon bond, with formation of carbon and isobutene, takes place independently of the formation of isoprene[14,115,116]. It is catalysed by both Brønsted and Lewis acid centres, but the chemisorption of dioxans on the Brønsted centres prevents this reaction[116]. Therefore variation in the number of Brønsted acid centres has a great effect on selectivity, whereas the total conversion is little affected by this factor.

In the cracking of alkyl-1,3-dioxans good yields of oxetans are obtained as well as dienes[89,124,125]. Under certain conditions oxetans can be prepared practically exclusively by means of this reaction[124]:



Little study has been made of the effect of the structure of the initial 1,3-dioxan on the course of reactions leading to the formation of oxetans. However, there are grounds for supposing that an important part is played by the symmetry of the dioxan molecule and the peculiar stability of the 3,3-dialkyloxetans formed in the series of alkyl-substituted oxetans[124].

The cracking of 4-methyl- and 4,5-dimethyl-1,3-dioxans on solid acid catalysts yields an alkylcarbinol[91,126] and isovaleraldehyde[127] depending on the space velocity, by the mechanism



VIII. CATALYTIC ISOMERISATION OF 1,3-DIOXANS

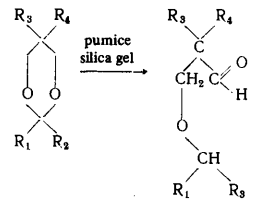
1. Heterogeneous Catalytic Isomerisation

The literature contains a large amount of experimental information on the heterogeneous catalytic isomerisation of 1,3-dioxans[125,128–131]. The isomerisation takes place by an ionic mechanism on weakly acid catalysts[125,128,129], and by a radical mechanism under thermal conditions[130,131].

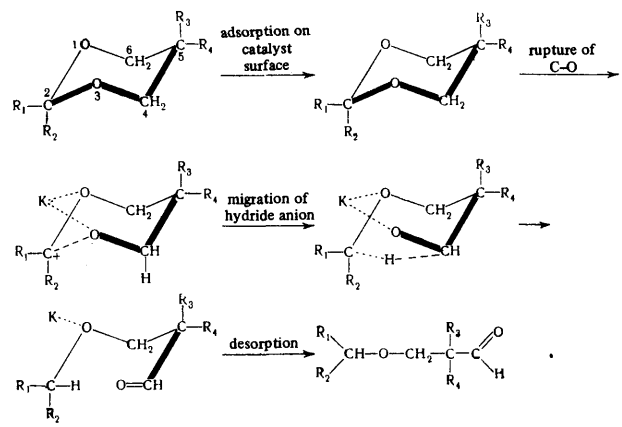
(*a*) Isomerisation by an ionic mechanism

Acid catalysts accomplish the cleavage of open-chain acetals with the formation of vinyl ethers and alcohols[132–139].

Rondestvedt and Mantell[125,128,129] note that 2,5,5-trialkyl-1,3-dioxans undergo isomerisation on pumice and silica gel into good yields of β-alkoxy-aldehydes:



The dioxan is assumed to be adsorbed on the acid centres of the catalyst in the chair conformation, and the resulting ionic compound is stabilised by migration of a hydride ion. The reaction mechanism can probably be represented by the scheme:



(i) Adsorption. Increasing the bulk of substituents prevents two-point adsorption of 1,3-dioxans. The size of the substituents R_1 and R_2 plays an especially important part. If R_1 in a dioxan ring in the chair conformation is considerably larger than R_2, it will occupy an equatorial position, which will prevent two-point adsorption of the dioxan on a catalyst surface, owing to repulsion of R_1 from the surface. The repulsion is eliminated on the migration of R_1 to the axial position. The energy required for such migration (1–4 kcal mole^{-1}) will depend on the difference in size between R_1 and R_2, and can be balanced by the difference in energy of repulsion between the substituents R_1, R_2 and the surface. If R_1 is an aromatic substituent, the attraction of its π-electrons to the acid centres of the surface will facilitate two-point adsorption. Electron-acceptor substituents in the aromatic ring, by diminishing the

electron density of the ring, prevent formation of a complex on the catalyst surface, whereas electron-donor substituents facilitate adsorption. Substituents containing unhindered oxygen and nitrogen atoms of basic character, located in the acetal ring, diminish the probability of oriented adsorption and thereby prevent isomerisation.

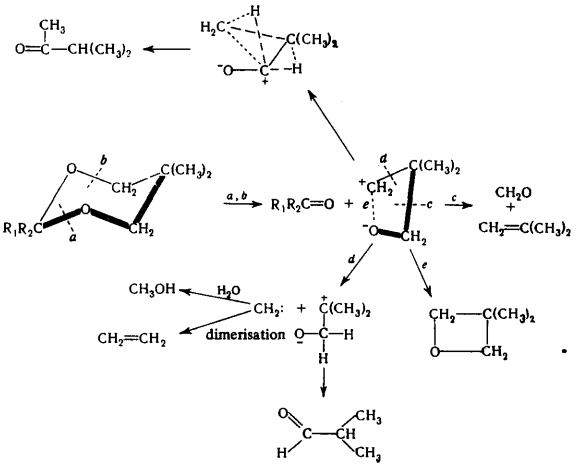
(ii) Rupture of carbon–oxygen bond and stabilisation of carbonium cation. The second stage of the reaction involves heterolytic rupture of the 2–3 carbon–oxygen bond with formation of a carbonium ion having the positive charge on the $C_{(2)}$ atom. The ability to form a cation depends on the size and the nature of the substituents attached to the $C_{(2)}$ atom. The diminution in the tendency of cyclic acetals to isomerise in the sequence—ketal > alkylacetal > formal—is associated with the formation and stabilisation of the carbonium cation, and serves to confirm the above hypotheses (see Sections II and III). The ease of isomerisation of 2-phenyl-1,3-dioxans depends on the nature of the *para*-substituent in the benzene ring. Electron-donor and electron-acceptor substituents respectively promote and impede isomerisation of 2-phenyl-1,3-dioxans, which in the absence of such substituents are extremely reactive.

The similarity in the first stages in the mechanisms of hydrolysis and isomerisation on weakly acidic catalysts (formation of a carbonium cation) explains the absence of isomerisation in 4,4-dialkyl-1,3-dioxans. Apart from obvious stereochemical considerations, it must be borne in mind that published data indicate[18,27] that 4-alkyl substituents facilitate cleavage of the 3–4 carbon–oxygen bond by diminishing the possibility of rupture of the 2–3 carbon–oxygen bond, which excludes the possibility of isomerisation. It must also be noted that the literature contains data on the successful isomerisation only of symmetrical 1,3-dioxans, for which cleavage of the 1–2 and 2–3 carbon–oxygen bonds is equally likely.

(iii) Migration of hydride anion from $C_{(4)}$ to $C_{(2)}$. Such migration accompanying cleavage of the 2–3 carbon–oxygen bond can be explained from the fact that aliphatic acetals form vinyl ethers on stabilisation of the carbonium cation formed during rupture of the carbon–oxygen bonds[132–139]. The cracking of six-membered cyclic acetals on weakly acidic catalysts yields alkoxy-aldehydes. In the latter case the catalyst ensures transfer of a hydride ion from $C_{(4)}$ to $C_{(2)}$, which is favoured also by the geometry of the intermediate complex. The constriction of the 1,3-dioxan ring at the oxygen atoms in the chair conformation brings the $C_{(2)}$ atom closer to the axial hydrogen atom attached to the $C_{(4)}$ atom, as a result of which the hydride ion migrates from $C_{(4)}$ to $C_{(2)}$ with cleavage of the 2–3 carbon–oxygen bond.

(iv) Desorption. The character of the transformation is greatly affected by the rate of desorption. A high rate at this stage favours smooth isomerisation, whereas slow desorption leads to resinification and deactivation of the catalyst. Thus the lone pairs of electrons in the case of 2-*p*-dimethylaminophenyl-1,3-dioxan or the presence of unhindered oxygen atoms in substituents in the dioxan ring prevent the isomerisation of these compounds owing to their strong adsorption.

Study of the secondary products enables conclusions to be drawn on the mechanism of the side-reactions. A detailed investigation of the products from 5,5-dimethyl-1,3-dioxan has shown that, besides the expected alkene and oxo-compound, catalysis yields substances whose formation can be explained by the scheme:

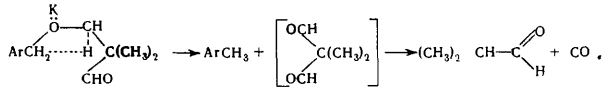


The main reaction via the zwitterion is (*d*), leading to the formation of isobutyraldehyde instead of the formaldehyde and isobutene expected according to reaction (*c*).

Besides compounds of the type $R_1R_2C:O$ (*a*–*b*) the reaction products were found to include formaldehyde, isobutene, isobutyraldehyde, isopropyl methyl ketone, $\alpha\alpha$-dimethylpropionaldehyde, methanol, 3,3-dimethyloxetan, ethylene, propene, and also hydrocarbons having a longer carbon chain than in the initial dioxan, with in rare cases vinyl ethers. Reaction (*e*) corresponds to closure of the zwitterion. Thus the ketal of cyclohexanone gives a 10% yield of the dimethyloxetan, whereas in the case of the initial ketal of cyclopentanone only traces of the dimethyloxetan were detected in the catalyst.

Under analogous conditions the seven-membered dioxetans are converted mainly into tetrahydrofuran derivatives, this reaction probably also involving the intermediate formation and closure of zwitterions. The detachment of a methylene radical by reaction (*d*) is confirmed by the presence of C_6 hydrocarbons among the products.

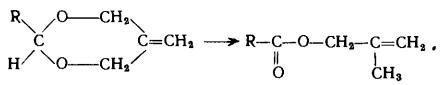
The by-products of the cracking of 2-aryl-1,3-dioxans include also toluene. The formation of toluene is probably accompanied by that of dimethylmalonaldehyde, which is decarbonylated to isobutyraldehyde:



It is very probable that benzaldehyde also is formed.

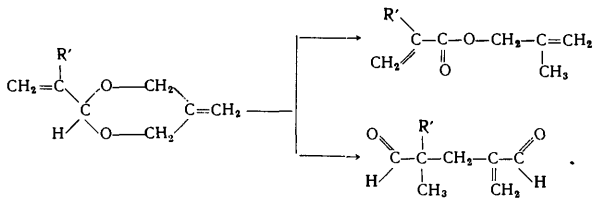
(*b*) Thermal isomerisation of 1,3-dioxans

An interesting case of the isomerisation of 1,3-dioxans on glass beads was observed by Weiss et al.[130,131], who found that with 5-methylene-1,3-dioxans the principal final products were methylallyl esters. Isomerisation into such esters is possible only with dioxans that contain a 2-hydrogen atom:



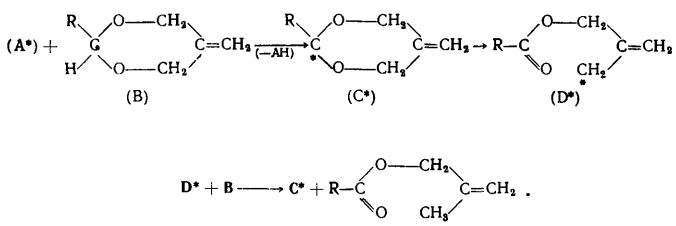
The nature of the 2-substituent has a fundamental effect on the character of the transformation of dioxans, but methylallyl esters are formed in all cases. If the substituent R

is a vinyl group, parallel formation of a dialdehyde takes place:

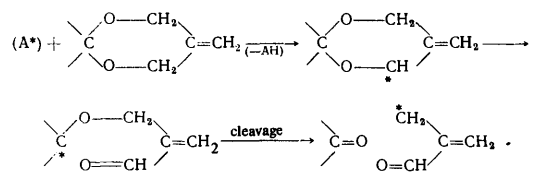


The presence of two 2-alkyl substituents stabilises the dioxan molecule. It must be noted that a radical mechanism has been suggested[140-146] for the conversion of acetals into esters. There appears to be no need[130] to introduce a free radical into the reaction medium to initiate the reaction, for the structure of the initial dioxan and diacetyl, containing double bonds of allyl type[130,131,140,141], creates favourable conditions for the occurrence of a radical reaction under the thermal conditions described.

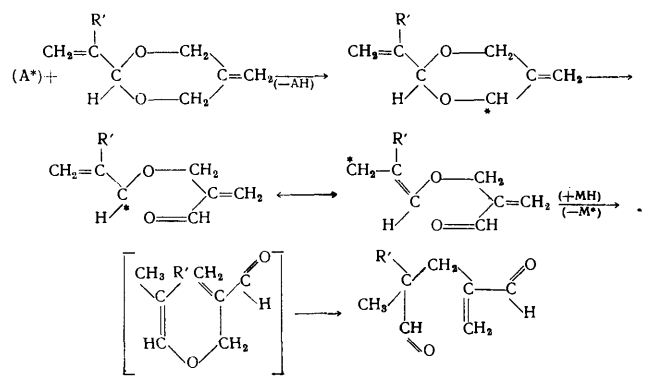
The reaction proceeds according to the scheme



The dioxan molecule undergoes cleavage if the primary act is attack on the quaternary carbon atom:

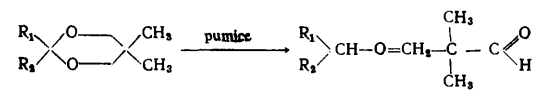


With 5-methylene-2-vinyl-1,3-dioxan as initial compound, however, analogous attack on the quaternary carbon atom leads to the formation of a dialdehyde:



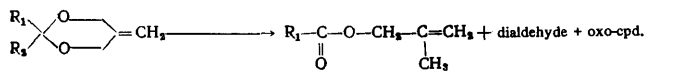
The possibility of the existence of an allyl vinyl ether—the hypothetical intermediate compound—represents a new concept in the field of radical reactions. Analogous views have been expressed earlier in the case of ionic reaction[147,148]. It is interesting to compare the results obtained by Rondestvedt[125,128,129] with those of Weiss et al.[130]. The tendency of 5,5-dimethyl-1,3-dioxans to isomerise increases with the structure of the initial oxo-component of the dioxans in the sequence—$\alpha\beta$-unsaturated aldehydes < aliphatic aldehydes < aromatic aldehydes < ketones—whereas 5-methylene-1,3-dioxans show an increase in activity in the reverse sequence—ketones < aliphatic aldehydes < aromatic aldehydes < $\alpha\beta$-unsaturated aldehydes[130]—see Tables 2 and 3. This is explained by differences in the structure of the 1,3-dioxans and in the mechanism of isomerisation.

Table 2. Ionic heterogeneous catalytic isomerisation.



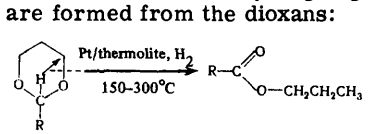
R_1	R_2	Unchanged dioxan, %	Yield based on dioxan converted, mole %		Isomerisation temp., °C
				$R_1-\underset{\underset{O}{\|}}{C}-R_2$	
$CH_2=CH-$	H	100	0	0	480
H	H	37	60	—	400—440
$(CH_3)_2CH-$	H	16	82	—	410
CH_3-	CH_3-	12	51	31	360
	H	0	>80	—	400
	H	0	75—80	5	400
	$-(CH_2)_5-$ O	0	80	10	390

Table 3. Radical heterogeneous catalytic isomerisation at 450°C.



R_1	R_2	Unchanged dioxan, %	Yield based on dioxan converted, mole %		
			methylallyl ester	dialdehyde	$R_1-\underset{\underset{O}{\|}}{C}-R_2$
$CH_2=C(CH_3)-$	H	8	39	13	47
$CH_2=CH-$	H	26.5	26	46	18
	H	41.5	79	—	17
$(CH_3)_2CH-$	H	58	97.5	—	1
	H	67	88	—	1.5
H	H	74	62	—	—
CH_3-	CH_3-	78.5	—	—	
	$-(CH_2)_5-$	100	—	—	0

An interesting possibility of isomerisation has been observed[149] with 2-alkyl-1,3-dioxans on platinum deposited on thermolite (1). In a stream of hydrogen good yields of propyl esters are formed from the dioxans:



2. Homogeneous Catalytic Isomerisation of 1,3-Dioxans

Esters are formed by the transformation of 1,3-dioxans in the presence of organic peroxides or by the action of ultraviolet radiation on these acetals[144,146]. The first stage in the reaction is regarded as involving detachment of hydrogen from the $C_{(2)}$ atom of the dioxan ring, this being followed by cleavage of a carbon–oxygen bond and formation of an ester molecule. 4-Methyl-2-phenyl-1,3-dioxan yields mainly n-butyl benzoate, the isobutyl ester being formed in smaller amount[144]:

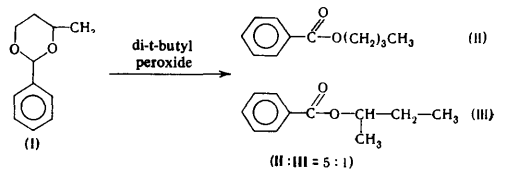
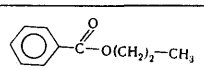
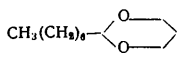
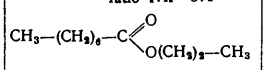
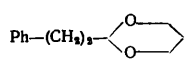
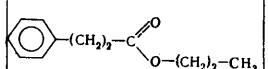


Table 4. Homogeneous catalytic isomerisation.

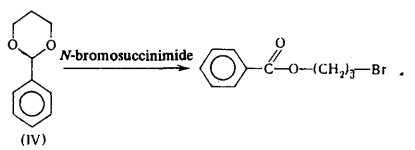
Dioxan	Catalyst	Reaction conditions	Reaction products	Ref.
IV	di-t-butyl peroxide	132°C 18 h		144
I	ditto	135°C 18 h	II III ratio I:II=5:1	144
	ultraviolet + acetone + t-butyl alcohol	20–40 h		146
	ditto	ditto		146

A similar distribution of products is observed in the isomerisation of mixed open-chain acetals in the presence of d-t-butyl peroxide, the course of the reaction being determined by the ability of the intermediate radicals formed to be stabilised by hyperconjugation[145]. Table 4 gives comparative data obtained for the isomerisation of 1,3-dioxans.

IX. POLYMERISATION AND OXIDATION OF 1,3-DIOXANS

The polymerisation, the copolymerisation, and also the oxidation of 1,3-dioxans have been very little studied. Strepikheev and Volokhina[150] investigated the possibility of their polymerisation in the presence of camphorsulphonic acid and obtained negative results. However, five-, seven-, and eight-membered cyclic acetals are in considerable measure polymerised under analogous conditions, the stability of the acetal ring increasing—and the tendency to polymerisation decreasing—with rise in temperature. These workers also found that the tendency to polymerise diminishes with decrease in the size of the ring in series of cyclic acetals, in the sequence—8 > 7 > 5 > 6—little difference in capacity for polymerisation being found between the five- and seven-membered rings. The enthalpy of cyclisation of acetals[151] also diminishes with the size of the ring, in the sequence 8 > 5 > 7 > 6. These results enable an assessment to be made of the relative tendency of cyclic acetals to polymerise.

The patent literature contains reports of the polymerisation and copolymerisation of 1,3-dioxans[79,152,153]. Peroxides, $\alpha\beta$-unsaturated esters, and their polymers have been obtained by the oxidation of 2-alkylene-1,3-dioxans in the presence of oxygen and cobalt(II) ions[154]. A good yield (~ 95%) of a benzoic ester has been obtained[155] by the reaction between *N*-bromosuccinimide and 2-phenyl-1,3-dioxan:



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Zelinskii Institute of Organic Chemistry, USSR Academy of Sciences, Moscow

Jozsef Atila University, Szeged, Hungary

U.D.C. 543.31

Methods for the Determination of Water in Substances in Different States of Aggregation

V.A.Drozdov, A.P.Kreshkov, and S.I.Petrov

The most important data on methods widely used at present to determine the concentration of moisture in substances in different states of aggregation are examined. The bibliography contains 715 references.

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I. INTRODUCTION

Since the publication of Mitchell and Smith's monograph[1], the Karl Fischer method for the determination of water has been improved, and new chemical, physical, and physicochemical methods for its determination, which have been widely used in various fields of science, industry, and the new technology, have been described.

Simultaneously, the requirements made of the methods themselves have become more severe, since the modern tendency in analytical chemistry is directed towards automation of the continuous control and regulation of technological processes, with minimal expenditure of effort on the actual analysis. This has led to the introduction and development of completely new and highly sensitive methods of analysis, such as infrared spectroscopy, coulometry, gas-liquid chromatography, etc.

Published reviews[2-30] of methods for the determination of water do not claim to examine this problem exhaustively.

In the present paper an attempt has been made to give a complete review of all methods for the determination of water in substances in different states of aggregation.

II. METHODS FOR THE DETERMINATION OF WATER BASED ON ITS SEPARATION

1. The Drying Method. The simplest and oldest method for the determination of water is based on the drying of the specimen to be analysed to constant weight. The water content is estimated from the loss in weight. The rate and efficiency of dehydration are determined by a number of factors: the way in which heat is supplied to the specimen being tested, the rate of removal of the water liberated, the establishment of an optimal temperature of drying, at which decomposition of the specimen being analysed is not observed[31,32], the state of the water molecules in the material being studied, and also diffusion conditions.

The drying process is influenced considerably by the depth of the layer and the friability of the specimen[33]. The reproducibility of the results depends on such factors as the design of the drying oven, the nature of the material from which the drying vessel is made, and the shape of the evaporation dishes. The rate of removal of water from the surface of a solid phase is a function of the water vapour pressure and the temperature of drying.

When moist organic substances are heated, changes in the weight of the substance being analysed may be due not only to the liberation of water, but also to the liberation of CO_2, CO, H_2, and CH_4. In the analysis of thermally unstable inorganic compounds (iron and aluminium sulphates), selective absorbers for water and sulphur dioxide are used.

The temperature at which the specimen is heated during drying is determined by the nature of the substance being analysed.

In addition to the determination of water of crystallisation in salts[34], the drying method can be used with different degrees of accuracy for the determination of the concentration of water in cheese[35], jam[36], sheeps' milk cheese[37], tungstosilicates[38], xanthates[39], wood[40,41], castor beans[42], grain and grain products[43,44], clay[45], natural glasses[33], cadmium thiobarbiturate[46], [iron ore] charges[47], carbon black[48], the raw material for opium[49], meat products[50], brown coals[51,52], nuts, raisins, and poppyseed[53], dried fruit[54], and malt[55].

In order to use lower temperatures for drying and hence prevent thermal decomposition of the specimen, the use of infrared radiation and reduced pressure has been proposed for the determination of water in salts[56,57] and serum[58,59].

By combining the drying oven and analytical balance, it is possible to determine losses in weight during drying, with elimination of the operations involving the transfer of the specimen to a desiccator, and the time required to cool the substance being analysed.

A number of authors have proposed the more rapid determination of water by the drying method using a combination of hot air circulation, infrared radiation, vacuum drying ovens, and special evaporating dishes. The methods cover the analysis of grain, starch, and foodstuffs[60-62], pharmaceutical products[63], fertilisers[64], grain and coffee[65], dried grapes[66], and hops[67].

New apparatus and procedures for studying the mechanism of the drying of colloidal capillary-porous materials have been published[68]. The British Standards Institute has published standards for vacuum drying ovens[69].

Various techniques[70], attachments, and automatic instruments for the determination of water by drying have been described[17,71-83].

The drying method has found most extensive application in the determination of hydrate water in inorganic compounds. The method is less satisfactory for organic compounds. The sources of error encountered in the drying method have been examined[84].

The drying method is time-consuming, has a low accuracy when the water concentration is low, and for practical utilisation it requires the establishment of standard conditions for each specific instance. A number of the proposed improvements (infrared radiation, vacuum drying apparatus, automatic balances, etc.), however, make it possible to reduce the time required for the determination of water to 15–20 min. The error in weighing determines the limit of the minimal quantities of water which can be detected. The chief disadvantage of the method is that it cannot distinguish between water and other volatile substances present. The drying method is irreplaceable, however, for the routine determination of water in heterogeneous materials (fresh fruit, grain, silage, etc.). The drying method can serve as a relative criterion in the development of new and improved methods for the determination of water.

2. The Sorption Method. The sorption method for the determination of water is based on the use of sorbents to trap water vapour removed by a current of carrier gas, with gradual heating of the substances being analysed. The absorption tube containing the sorbent is weighed before and after the passage of the carrier gas, and the increase in weight gives the water concentration.

Various solid and liquid reagents have been used as absorbents: $CaCl_2$, P_2O_5, $CoCl_2$, drierite, anhydrone, sulphuric acid phosphoric acid, etc. The characteristics of various drying agents have been compared[85].

Dry air or argon are often used as carrier gas. The choice of carrier gas for a particular example of the determination of water is determined by the nature of the substance being analysed.

The sorption method is used for the determination of water in liquid and gaseous chlorine[86], liquids[87], silicate and carbonate minerals[88,89], beryllium carbide[90], wool[91], and potassium fertilisers[92], and for the determination of oxides and water in metal powders[93] and cable insulating paper[94]. In the simultaneous determination of water and CO_2 in rocks and minerals[89], a mixture of sodium carbonate and asbestos is used as absorbent to trap CO_2.

The sorption method is regarded as superior to the drying method, but it is very tedious and time-consuming, and cannot be automated. The accuracy of the method depends on the nature of the substance being analysed, the concentration of water being determined, the sensitivity of the analytical balance, and the selective absorbing power of the sorbent. By varying the absorbent, it is possible to carry out the separate determination of water and thermal decomposition products. The sorption method is also used as a means of separating water for its subsequent determination by chemical and physicochemical methods.

3. The Distillation Method. A weighed specimen of the substance being analysed is boiled in a special apparatus with an excess of a liquid which is immiscible with water (C_6H_6, toluene, xylene, CCl_4, tetrachloroethane, dioxan, perchloroethylene, aniline, mineral oils, petroleum fractions, etc.). The mixture of vapours distilled is condensed in a special distillate receiver, the liquids separate into layers, and the volume of distilled water is read off from the meniscus. The choice of solvent and the time for which the specimen is boiled are determined by the ease with which the boiling liquid penetrates into the pores of the finely ground specimen. The solvent chosen should distil in the form of an azeotropic mixture at a temperature at which chemical reactions do not take place. By creating an inert gas atmosphere in the distillation apparatus it is possible to avoid redox processes.

The accuracy of the determination of water by the distillation method depends to a considerable extent on the design of the condensate trap and the boiling assembly. Various trap designs cater for instances when the boiling liquid is lighter or heavier than water. Highly accurate results can be obtained by fine graduation of the measuring vessels and by placing the traps in a thermostat. In order to reduce the consumption of solvent during the determination and hence decrease the error in the determination due to the mutual solubility of the liquids, traps capable of returning part of the distilled liquid, after separation into layers, into the boiler assembly have been proposed.

The use of different solvents makes possible the separate determination of moisture and water of crystallisation in the same material. When azeotropic distillation with benzene and xylene are used for calcium sulphate and superphosphate fertiliser specimens, both free water and water of crystallisation are removed using xylene, whereas only free water is removed using benzene[95].

The time required for the distillation varies from 15–30 min to several hours, and is determined by the properties of the material being studied (solid or liquid, degree of subdivision, solvent chosen, temperature of distillation, etc.).

An extensive review of literature on the distillation method has been given in a paper[96] which describes the history of the development of the distillation method, gives various designs of distillation assembly, and examines critically a large number of practical examples of the use of the method. The construction of apparatus for the distillation is being constantly improved[96-108].

Satisfactory results have been given by the distillation method in the determination of water in soap[109-111], printing dyes[109], sugar-containing products[112], food products[113-115], silage[116], gypsum and superphosphates[95], furfural[117], diesel fuel, petrol, and sump oils[106], glycols and glycerol[118], diethylene glycol[119], polyethylene glycol[120], textile materials[101], petroleum and petroleum products[121], polycaprolactam[122], and DDT and HCCH emulsions[123]. A USSR State Standard has been published on the distillation method[124].

The distillation method uses simple apparatus, and all the operations are straightforward. Analytical chemists often use this method when the drying and sorption methods are inapplicable, and also when it is necessary to obtain comparative results in the development of new methods for the determination of water. In the last instance, the distillation method serves as a criterion. When the concentration of water in the substances being analysed is low, the distillation method is combined with other chemical and physicochemical methods of analysis.

III. METHODS FOR THE DETERMINATION OF WATER BASED ON THE USE OF CHEMICAL REACTIONS

1. Gas-volumetric methods. Calcium hydride reacts vigorously with water with the liberation of hydrogen, which can be measured quantitatively by volumetric or manometric methods. If the water to be determined is first extracted with a solvent, the reaction can be used for the quantitative determination of water. The solvent should be inert towards CaH_2. The first material to be proposed as extracting agent for water was degassed ethanol[125-127], and this was subsequently replaced by dioxan and pyridine[128,129].

Calculation of the thermodynamic potentials of the CaH_2–H_2O system has shown [130] that different quantities of hydrogen are liberated, depending on the temperature. In gas-volumetric determinations, strict control of the conditions of the analysis is necessary. The method can then be used for the quantitative determination of water with satisfactory accuracy in a variety of substances: inorganic crystal hydrates, liquid fuels, furfural, petroleum products, uranium hexafluoride, etc. [131-139]. The determination of traces of water vapour in gases has been described [140]. The calcium hydride method is the subject of a USSR State Standard [141].

The formation of acetylene by the reaction of water with CaC_2 has been made the basis of a method for the determination of water in substances in different states of aggregation. Since alcohols react with CaC_2 to form C_2H_2, they are unsuitable for use as media in the analysis. Inert solvents are recommended. The quantity of acetylene liberated can be measured by gas-volumetric methods, from the increase in pressure in the system, from the loss in weight of the reagent after volatilisation of the C_2H_2, by flame intensity measurements, or by measuring the quantity of oxygen required for combustion of the acetylene. In a number of instances it is considered more rational not to carry out the reaction between CaC_2 and the water-containing liquid in a heterogeneous system, and the preliminary extraction of the water by an inert carrier gas is recommended.

The carbide method for the determination of water has a number of disadvantages and limitations [130,139,142] and requires strict control of the conditions during the analysis. The method is used for the rapid determination of water in various materials: liquid coking and pyrolysis products [136], furfural [117], ores, brown coals [143], gypsum [144], rubber [146], ethyl acetate and chloroaldehyde [146], soils and building materials [147], industrial oils [148], cresol [149], metallurgical slags [150], hydrocarbons [151], leather, paper [152], grain [152,153], groats [154], peat, and wood [155].

The carbide method cannot be used for the determination of water in substances which react with CaC_2, CaO, or $Ca(OH)_2$.

Some authors consider that magnesium nitride is more convenient for the analysis than CaC_2, since the ammonia formed can be determined quantitatively by acid-base titration. Ethanol, dioxan, and a CH_3OH–C_2H_5OH mixture have been recommended as media. The analysis can be carried out in an ordinary Kjeldahl apparatus. High accuracy can be achieved in the determinations if the water is removed beforehand from the materials being studied, using a carrier gas. The method cannot be used to analyse substances which liberate NH_3 when heated. Temperature has a significant influence on the course of the reaction between Mg_3N_2 and water [130].

Noteworthy papers have been published on the use of magnesium nitride for the determination of water in divinyl distillate [156,157], gases [158], spirits and eau de Cologne [159], and transformer oil [160].

Tserevitinov's method for the determination of active hydrogen has been modified for the determination of water. The substance to be analysed is dissolved in pyridine or other inert solvent which does not react with CH_3MgI. Various compounds which contain active hydrogen atoms or which react with the Grignard reagent interfere in the determination of water. Tserevitinov's method has been proposed for the determination of water in oil [161] and gypsum [144].

Among other gas-volumetric methods, mention must be made of the determination of combined water in silica gel using diborane [162] and in solvents using alkali metals and their alloys.

Gas-volumetric methods (particularly the carbide and hydride methods) are distinguished by the rapid reaction of the reagent with the water being determined, and they have found extensive application in technology, as a result of the variety of methods for measuring the gas liberated. The required speed, accuracy, and sensitivity can be achieved.

2. Titrimetric Method. The Karl Fischer method [1] occupies a unique position among titrimetric methods for the determination of water. Study of the nature of the Karl Fischer reagent has established [163-165] that the quantity of methanol taking part in the titration has a significant influence on the results of the water determination. The titre of the reagent is a function of the ratio $H_2O : CH_3OH$. It has been proved experimentally [166] that for a solution of the reagent containing no methanol the ratio of the reacting I_2 and H_2O is 1 : 0.53, and that this ratio increases when CH_3OH is added. At a CH_3OH concentration of 24 vol.%, the ratio is equal to 1 : 1.5, and it subsequently remains almost constant over a considerable range (as far as 70%). When the reaction medium contains a large quantity of CH_3OH or C_5H_5N, additional complications, depending on the quantity of water being titrated, are observed. The deviations from the ratio 1 : 1.5 are greater, the smaller the quantity of water being titrated. The following equation has been proposed [11]

$$2H_2O + 4CH_3OH + 3C_5H_5N \cdot SO_2 + 3I_2 + 6C_5H_5N \rightarrow$$
$$\rightarrow 2C_5H_5N\begin{matrix}CH_3\\SO_4H\end{matrix} + C_5H_5N\begin{matrix}CH_3\\SO_4CH_3\end{matrix} + 6C_5H_5N \cdot HI .$$

The observed dependence of the water equivalent of the Karl Fischer reagent on the ratio $CH_3OH : C_5H_5N$ requires that the titration be carried out correctly. The standardisation of the Karl Fischer reagent and the determination of water must be carried out in a methanol + pyridine mixture with the same composition as that used for the Karl Fischer reagent. The value for the blank titration of the solvent cannot be found by titrating a smaller quantity and then multiplying the results of the titration by an appropriate factor.

The Karl Fischer reagent is prepared by mixing all the components together at the same time [1,166] (in this instance, however, the reagent may undergo a considerable loss of activity during storage [167]) or by mixing methanol and pyridine solutions of sulphur dioxide and iodine before use [168-172]. To decrease the time required for the preparation of the reagent, a simplified method for dehydrating the components with bromine or chlorine has been described [173]. It has been recommended [168] that the titration be carried out by dissolving the specimen to be analysed in a pyridine–methanol solution of sulphur dioxide. The titrant is a methanol solution of iodine.

A large number of attempts have been made by research workers to replace the components of the reagent in order to make it cheaper and to achieve greater stability. The replacement of pyridine by hexamethylenetetramine has been proposed [168], but sparingly soluble reaction products are formed. The replacement of methanol by the monomethyl ester of ethylene glycol [174] gives a more stable reagent, which has been shown to have valuable qualities [175]. It has been reported [176] that methanol can be replaced by chloroform. The preparation of an improved and stabilised reagent has been described [177].

For work in inert solvents (dioxan, benzene, CH_3CN, etc.), the use of a chloroform solution of bromine and sulphur dioxide has been proposed [178]. Substances containing HO-groups cannot be titrated with the recommended reagent. Pyridine and HCOOH also interfere.

The preparation of an improved reagent [179], designed for the determination of water in caprolactam and alcohols [180,181], has been patented. An alkoxide, phenoxide, or salts of organic acids are added to the reagent to combine with the hydrogen ions formed during the analysis. Patents [182-184] have recommended the addition to the reagent of one or more of the products of the spontaneous reaction which takes place in the reagent in the absence of water (NaI, pyridinium hydrogen, di-iodide, and secondary or tertiary amines).

The working solution is standardised by titrating accurately weighed specimens of H_2O in an inert solvent [163,164] or mixed solvent $C_5H_5N + CH_3OH$ (3 : 7) [11]. If the reagent is standardised using a standard solution of water in methanol, the determination gives its apparent water number [185], which may not coincide with the true value. It is recommended that the modified reagent be standardised using accurately weighed specimens of water or by titrating accurately measured volumes of aqueous solutions of methanol or ethanol.

Crystal hydrates have been used to standardise the Karl Fischer reagent [1,186,187].

Allowance must be made for the temperature factor [188] when the temperature of the surrounding medium during the standardisation differs from the temperature at which the analysis is carried out.

Methanol and its mixtures with pyridine, ether [189], chloroform [190], or propanol [172] are most frequently used as media for the titration. Ethylene glycol and glycerol are used only if it is necessary to determine water in gases after its absorption by these solvents. Dioxan has also been recommended [163,164,191,192]. Chloroform is usually employed for substances insoluble in methanol [193-195]. Toluene is used [196] if water is being determined after azeotropic distillation. Formamide [197], because of its high dielectric constant, is an excellent solvent and extracting agent. Acetic acid [170,197] or its mixtures with pyridine [198] are used for special purposes.

The use of *N*-ethylpiperidine as catalyst to increase the rate of the reaction between H_2O and the titrant has been recommended [199].

The analytical control of the Karl Fischer reagent has been described [200]. The spent reagent can be regenerated [11].

A variety of methods are used to detect the equivalence point in the titration. The technique of visual titration has been described in detail [1]. A new feature in this field is the attempt to introduce indicators [201-203]. Various modifications of the visual titration technique have been examined [204,205].

A photometric method for the detection of the equivalence point has been proposed for the determination of water in coloured liquids [167,206-209].

Electrometric titration is widely used to detect the equivalence point. Direct and back potentiometric titration using a bimetallic electrode couple has been described [1,210]. The so-called "dead stop" method of titration is most widely used [1,211,212]. The mechanism of the titration using polarised electrodes has been examined [213]. The sharp change in current strength at the equivalence point can be recorded using a qualitatively-operating electric eye [214]. The development of electronic apparatus has led to the production of various automatic assemblies [215-220].

There is a wide range of apparatus for electrometric Karl Fischer titration [216-234] by macro-, semimicro-, and micro-methods with complete or partial automation. In addition to standard cells attached to the titrator, various original modifications of the cell vessels and pipettes have been described [222,235-241].

Coulometric titration with the Karl Fischer reagent, based on the electrolytic generation of iodine, has been recommended for the automatic continuous control of traces of water [242-252].

Titration with the Karl Fischer reagent is used for the determination of water in various forms in the following inorganic substances: liquid ammonia [1,253], hydrogen fluoride [254,255], crystal hydrates [182,256], concentrated sulphuric [204] and nitric acids and their mixtures [257,258], ammonium perchlorate [259], uranium tetrafluoride and uranium oxide [260], mineral pigments [261], contaminated acids in sulphonation processes [262], minerals [263], calcium chloride [264], titanium(III) and vanadium(III) chlorides [265], pigments and paints [266,267], sodium tetraborate [268], granulated fertilisers [269-271], the inorganic components of solid rocket fuel [272], complex salts [273], inorganic reagents [274], and sulphuryl chloride derivatives [275].

In the determination of water using the Karl Fischer reagent, it is necessary to make allowance for the reaction of the components of the reagent with various inorganic compounds [1,261]. Thus in the determination of water in iron(III) salts a redox reaction takes place, but this can be prevented by adding 8-quinolinol [276] and carrying out the titration in quinoline.

The total concentration of water in sulphuric acid is usually determined by titrating in pyridine or a mixed pyridine + dioxan solvent, in order to reduce to a minimum the participation of methanol in the reaction. Water in fuming nitric acid is determined by titration in dimethyl formamide + pyridine [257] or dichloroethane [258]. An original method has been proposed for the determination of water and alkali metal oxide with selenium and tellurium [277].

Unsatisfactory results are obtained in the direct titration of anhydrous sodium carbonate [278], sodium carbonate, borate, and perborate, glycerophosphate, $CaCO_3$, calcium and magnesium oxides, hydrogen carbonate [63], acid salts, and $CuSO_4.5H_2O$ [279]. In these instances, preliminary xylene distillation of H_2O or its extraction with methanol [280], tetrahydrofuran, or dioxan [279] are recommended. The quantity of basic substance passing into solution during extraction is determined by titration with acid.

It is possible to determine water by direct titration in a number of organic compounds: salts of organic acids [164], sodium alkylarylsulphonate [281], dynamite glycerol [282], amines and amides [1,166,204], rubber [283,284], medical raw materials [285], pharmaceutical products [286-292], alkaloids [170,175,288], antibiotics [288,293,294], vegetable oils [195,295,296], solvents [171,204,264,297,298], powders and explosives [272,282,292,300], petroleum and petroleum products [301-303], insulating and lubricating oils [304-306], insecticide aerosols [307], oils and fats [195,261], aviation fuel [190], xanthates [308], potassium xanthate [168], cellophane [208], polymers and plastics [292,309-311], polyvinylpyrrolidone [312], vitamin C [168], milk powder and cheeses [313], starch [197,314], leather and tanning agents [315-317], dried vegetables [197,318], grain products [25,319], textile materials [320,321], soap and wetting agents [322], coals [204,323], formaldehyde polymers with low molecular weight [324], seeds [325], treacle [326,327], honey [328], cocoa [329], chocolate [330], flour and flour products [331,332], hydrocarbons [303], glycol and glycerol frost-resistant solvents [118], vinyl esters [322], ketones [234-336], tributyl phosphate and kerosene [337], ion exchange resins [338], laminated polyamides [339], aerosol coatings [340], malt [55], serum [59], gelatin [341], and alginates [342].

The determination of water by the Karl Fischer method in aldehydes and ketones requires appropriate modifications [1,334-336,343]. Ascorbic acid is oxidised by the reagent to dehydroascorbic acid, and quinone is reduced to hydroquinone. Thiols are oxidised slowly, but their influence can be eliminated by adding alkenes before the titration.

Various silanols react quantitatively with the Karl Fischer reagent [344,345]. The determination of H_2O in silicones in the presence of silanols has been examined [346].

In the determination of water in gases, for example hydrocarbons [347-350], hydrogen chloride [351], the atmosphere of furnaces used for the annealing of porcelain and enamel [352], oxygen, nitrogen, and other gases [350,353], the gases are bubbled through anhydrous methanol and the absorbed water is determined by titration.

In evaluating the Karl Fischer titration, it should be noted that the method is applicable to the direct determination of water in quantities varying from one part per million to 100% in all types of compound which do not react with the components of the reagent. In order to achieve the highest sensitivity in the determination, it is recommended that the solvent (preferably a pyridine + methanol mixture) be titrated first, followed by analysis of the specimen in the same medium. Direct titration gives the total concentration of water (free and combined). The Karl Fischer titration is readily automated. The coulometric method for the generation of iodine for the Karl Fischer reagent has made possible the continuous automatic regulation and control of moisture content in industry. In view of the universal and highly sensitive nature of the method, it is often used as a standard in the development of new methods for the determination of moisture.

Among other titrimetric methods, mention must be made of those based on the reaction of water with various inorganic chlorides and organic acid chlorides. The hydrogen chloride liberated is distilled off and titrated. Of the readily hydrolysed chlorides, aluminium chloride has proved the most suitable.

The acetyl chloride method [354] is convenient for the determination of water in substances which present difficulties in the Karl Fischer method. The method is based on the difference in the behaviour towards water and alcohol shown by acetyl chloride, prepared in dioxan, toluene, or CCl_4. In the first instance, 1 mole of water liberates 2 moles of titratable acids (CH_3COOH + HCl) whereas in the second instance 1 mole of CH_3OH liberates 1 mole of acid (HCl). When the reaction of the reagent with water-containing inert solvents is complete, the excess of CH_3COCl is treated with alcohol and titrated with alkali solution. A blank titration is carried out for the calculations.

The method is used to determine water in liquid hydrocarbons, esters [354], gaseous hydrocarbons [355], acetone [354,356], edible oils, margarine, and fats [357], alcohols [358], and coals [359].

CH_3OH cannot be used as extracting agent in the acetyl chloride method, because it reacts with CH_3COCl. Formic acid, aldehydes, and high concentrations of lower alcohols and glycols interfere in the determination. Strong amines and esters which are readily hydrolysed in the acidimetric titration may distort the results of the analyses considerably.

The use of *p*-nitrobenzoyl chloride [360], lauryl chloride, stearyl chloride, or benzoyl chloride in place of acetyl chloride has been proposed, but these are not all successful. Studies have shown [361] that the addition of organic bases facilitates the rapid and quantitative hydrolysis of acid chlorides by water.

Succinoyl dichloride has been used as hydrolytic reagent for the determination of the water content of gases and crystal hydrates [362,363].

The hydrolysis of acid anhydrides and chlorides can be used for the determination of water. The use of acetic [364] and benzoic anhydrides for this purpose has been described. The water to be determined is collected in a 1:3 anhydride + pyridine mixture by azeotropic distillation, for example with dioxan or toluene, after which the hydrolysis is carried out and the excess of the anhydride is eliminated using aniline. A blank titration is carried out for the calculation. The time required for the hydrolysis is reduced considerably if catalysts ($HClO_4$ or 2,4-dinitrobenzenesulphonic acid [365]) are added to the reaction mixture.

The reaction of sodium alkoxide with water has been used to determine small quantities of water in alcohol, dioxan, crotonylidene-acetone, and anthraquinone [366]. The sodium hydroxide liberated reacts further with ethyl acetate to form CH_3COONa, and the excess of sodium alkoxide is determined by titration.

Lead tetra-acetate in benzene solution reacts with water to form PbO_2, which is determined iodometrically [367].

Organic compounds of the alkali metals (triphenylmethylsodium) react vigorously with water. Since organic compounds of the alkali metals are coloured, and the products of their reaction with water colourless, water can be titrated without using indicators [368].

By making use of the limited mutual solubility of the liquids in the presence of water, it is possible to determine water in furfural by titration with a mixture of hexanol and cotton-seed oil [369], in blood and biological materials with xylene [370], and in crystal hydrates with a mixture of C_2H_5OH and 2-methylpropanol [371]. Extensive material on the determination of the moisture content of substances by titration of the water has been published [372].

Papers have been published on the determination of water in organic compounds by a new chemical method based on the hydrolysis of t-butyl vanadate in the presence of NH_3 or acridine [373,374]. The precipitate formed in the reaction—a salt of vanadic acid—is determined by titration with a solution of Mohr's salt. The method can be used to determine water in hydrocarbons, alkyl halides, esters, ketones, benzaldehyde, and pyridine. A semi-automated version of the method has been proposed.

A method for the determination of water in alcohols has been developed, based on the hydrolysis of dimethyl oxalate in alkaline solution [375].

Water can be determined by acid-base titration in non-aqueous media. Thus water has been determined by titration in anhydrous sulphuric acid [376,377]. $HClO_4$ was used as titrant.

Other titrimetric methods have found less extensive practical application than the Karl Fischer method, due to the characteristic features of the reagents. The most widespread is the acetyl chloride method, use of which is recommended when the Karl Fischer method is inapplicable. The most promising method is that based on the hydrolysis of t-butyl vanadate.

3. Gravimetric Methods. Methods for the quantitative determination of water have been based on the water-removing properties of anhydrous copper sulphate (in alcohols, aldehydes, and acids). Aluminium and magnesium ethoxides react with water to form equivalent quantities of the hydroxides, which are determined by weighing. Large quantities of water in alcohols and in mixtures of alcohol with benzene, petrol, and trichloroethylene are determined by making use of the hydrolysis of

ethyl formate. The product is weighed as sodium formate.

The determination of water in bromine is based on the oxidation of sulphur dioxide by bromine in the presence of water. The sulphate formed is determined gravimetrically [378].

Water at concentrations of 10–100 mg per 100 ml specimen can be determined in the organic solvents ether, $CHCl_3$, CCl_4, and hydrocarbons using an ethereal solution of LiBr, which reacts with water to precipitate $LiBr.H_2O$, determined by weighing [379].

An automatic gravimetric hygrometer for the determination of moisture in gases has been described [380].

Gravimetric methods find only limited application, because of the tedious nature of the operations, the time required, and the specific character of the method.

IV. PHYSICAL AND PHYSICOCHEMICAL METHODS FOR THE DETERMINATION OF WATER

1. Methods Based on Measurement of the Specific Gravity, Viscosity, Angle of Rotation of Polarised Light, Refractive Index, Mutual Solubility, Etc. Methods recommended for the determination of water have been based on measurement of the specific gravity of the substance being studied (determination of water in alcohols [381]), measurement of the viscosity (in acetone, alcohol [382], concrete, cement, and other building materials [383]), and the ability of an optically active water-containing substance to rotate the plane of polarisation of plane-polarised light to an extent proportional to the water concentration (determination of water in sugar refinery pulp [384] and in sugar [385]). A refractometric method can be used to determine water in two- and three-component systems (analysis of furfural [117], sugar products [54,386], mixtures of formaldehyde and HNO_3 [387], and C_2H_5OH and ethyl cellosolve [388]). Methods of analysis making use of the difference in the temperatures of boiling sugar sap and the vapour [389], the thermal conductivity of gases [390], the critical temperature of mixing of liquids (determination of water in aniline [391]), the change in pressure accompanying the freezing of water (in air [392] or gases [393]) and the change in the specific enthalpy of the moist material during the desorption of water [394] have been described. Surface moisture can be determined by weighing the specimen in air and in two liquids which have different densities and which are miscible with water [395,396].

In the determination of the moisture content of gases, extensive use is made of the "dew point" method [397,398], for which a large number of instruments, constructed on different principles, have been described: with thermoelectric cooling [399,400], with cooling in a Dewar vessel [401], pneumatic [402], with electrical contact [403], and with photoelectric recording [404]. A method [405] and apparatus [406] for controlling the moisture content of organic solvents, based on measurement of the concentration of water in the vapour above the solvent, have been patented. The moisture content of board and other porous materials is determined by measuring the equilibrium vapour pressure [407].

In the utilisation of the psychrometric method for the determination of the moisture content of gases, particular attention is being paid to the theoretical principles of the method [398,408], particularly at high temperatures [409]. Various psychrometers have been described [404,410-412].

2. Methods Based on Measurement of the Dielectric Constant. The determination of H_2O in various materials is based on measurement of the dielectric constant (DC) of the system. The DC of water (80.57) differs significantly from that of other solvents. The theoretical principles of the method based on DC measurements have been described [413,414]; the empirical relationship $DC = f(H_2O)$ is used for each specific water-containing system. The sensitivity of the determination when the DC of the solvent is sufficiently constant may reach several parts per million. Measurements of the DC losses are more sensitive.

For the determination of water in hydrocarbons, dioxan, which is a common cosolvent for H_2O and hydrocarbons, is recommended, since the DC of dissolved and emulsified water are quite different [415]. Measurements of the DC of an emulsion of NaOH solution in transformer oil have been given [416]. The method is widely used to control the concentration of water in petroleum and petroleum products [417-426]. Continuous measurement and recording are possible even at water concentrations reaching 60% [427]. The measurements are often carried out by comparing the DC of water-containing petroleum and anhydrous petroleum [428-430]. The determination of water in hydrazine and phenylhydrazine [431], monohydric and polyhydric alcohols [432], pyridine bases [433], ethyl acetate [434,435], dioxan [433], the diethyl ether of diethyleneglycol [436], the three-component methanol–propan-2-ol–water system [437], and mineral oils [438] has been described.

For multi-component systems, determination of water by loss measurements is in most instances impossible, since the dielectric loss factor may be altered for reasons other than a change in the water concentration [413].

To determine water in solids, use is made of preliminary extraction by a solvent [414], for example in the determination of water in soil [439], spinach [440], quartz sand, manganese ores, coal, clay [441], wheat, ammonium sulphate, etc. [442]. The limits of applicability of the method involving preliminary extraction are made narrower when the extracting solvent does not extract water completely, or when complete extraction takes a long time. This has led to the development of the immersion method [443]. The substance being analysed is immersed in a liquid with known DC value, and the final DC of the system is measured. The H_2O concentration is found from a calibration curve. This method has been proposed for the analysis of inorganic fertilisers [443,444].

Water can be determined in many materials by immersing electrodes directly in the substance being studied: molecular sieves [445], grain [445-448], hops [446], peat [449], soil [450], packing materials [451], tobacco [452-454], [iron ore] charges [455], textile fibres [456], loose materials [457,458], moulding mixtures [459,460], paper and cardboard [461], granulated materials, Nitrophos [462], and trinitrotoluene [463]. In some instances it is necessary to keep the pressure of the electrodes on the material being studied strictly constant [452].

The dielectric loss method is particularly promising for the analysis of loose materials. Thus it is possible to measure the moisture content of pigments without weighing a specimen [413].

Special cell designs have been developed, making it possible to determine the concentration of water in films [413,464]. A portable hygrometer for the determination of the moisture content of air from DC measurements has been described [465,466]. An analyser for the continuous determination of moisture in gases containing HF has been described [467].

Various types of apparatus for carrying out the determination have been described [17,421,468-475].

3. Methods Based on Measurement of the Electrical Conductivity. The moisture content of

gases absorbed by a solvent is determined by measuring the electrical conductivity of the water-containing extracting agent [476]. Sulphuric acid is used as absorbent for the moisture in natural gas [477]. The electrical resistance of LiCl is a function of the moisture content of the gas in contact with the salt [478].

The moisture content of soil [479] is determined by measuring the electrical resistance of a mixed solvent saturated with NaCl after the extraction of water from the soil. The measurement of the moisture content of transformer oil from the change in the electrical resistance of a fabric placed between perforated metal plates has been described [480]. Specific resistance measurements have been used for the continuous control of the moisture content of the rocket fuel dinitrogen tetroxide [481]. The method involving electrical conductivity measurements has been used to determine water in liquids—hydrogen fluoride [482,483], propane [484], petroleum residue [485], and pyridine [486].

The continuous determination of the electrical conductivity of solids can be carried out usually at high water concentrations. The electrical conductivity depends on the source voltage, the shape and arrangement of the electrodes, the chemical composition of the material, temperature, the degree of uniformity, the state and the distribution of the water, the degree of polarisation, the state of the surface of the individual granules and pieces and the degree of compactness and contact in the material [17]. Methods and apparatus have been described for the rapid determination of moisture from electrical conductivity measurements in sawn timber and wood [487-489], salt [490], leather [491], chromium oxide [492], paper, textiles [493], peat [494], copra [495], and chromatograms [496].

In radiosondes, moisture is determined using a hygrometer element of oxidised aluminium, whose resistance is a function of the moisture content of the atmosphere [497].

Various forms of apparatus have been described [10,17,21,469-471,488-501].

4. Electrometric Methods. The coulometric method is based on the determination of the quantity of electricity required for the electrolysis of water absorbed by a thin film of absorbent (H_3PO_4, H_2SO_4, or their mixtures, P_2O_5, KOH, K_2CO_3, etc.) [502-511] from a measured quantity of gas. In the analysis of liquids [503,512-515] and solids [17,503], the water is first transferred to the gaseous phase by evaporation or by using a current of heated dry gas [512]. The quantity of current used in the electrolysis is recorded graphically from a curve giving the change in current, by means of integrators [17,514], or from the magnitude of the current [515]. The rate of carrier gas [flow] depends on the design of the recorder, the nature and moisture content of the specimen, and the weight taken. For solids, a method involving the extraction of moisture by a gas, combined with heating by high-frequency currents, has been described [17,512,513].

Procedures [516,517] and apparatus have been described for determination of moisture by comparing the pressures of the gas being analysed and a reference gas for the same resistance of the hygroscopic film.

The efficiency of analysers for the determination of water in gas streams and liquid streams has been studied [518].

The coulometric method can be used to determine water in cracking gases, petrol vapour, natural gas [504,519], air [520], aromatic hydrocarbons [521], organic liquids [512,514,516], the technological product streams in petroleum refineries [522], circulating freon refrigerant [516,517], and solids [523,524].

Water in ϵ-caprolactam can be determined polarographically [525,526]. It is suggested that water in various organic compounds can be determined by the reaction of the substance with phenylchloro-oxophosphorus, which leads to an increase in the polarographic current of the solution at a given potential [527]. An improvement of the method has also been determined [528].

5. Optical Methods. Water in liquid products can be detected qualitatively using indicator paper [529-531] impregnated with salts $CoCl_2$, $CuBr_2$, BiI_3, SbI_3 or mixtures $K_3Fe(CN)_6 + CoCl_2$, $K_2CrO_4 + MnCl_2$ + resorcinol, activated silica gel treated with $CoBr_2$ solution [532], or molecular sieve A [533].

The change in the colour of solutions of a number of compounds as a result of hydration of the reagent can be used for colorimetric analysis. Thus cobalt compounds can be used to determine water with satisfactory accuracy in $CHCl_3$, salicylaldehyde, crotonaldehyde, and benzaldehyde [534], acetone [534-536], Cl_2CF_2, Cl_3CF, $ClCF_3$, petrol, methyl chloride [537], refined sugars [538], alcohols, acetone, ethyl acetate [539], maize, and Indian corn [540]. Water in solid specimens is extracted beforehand using a solvent.

With increase in the concentration of water in alcohol, there is an increase in solubility and a development of the colour of $K_2Cr_2O_7$ [541], and in reactive fuels, hexachlorane, and turbine oils a similar effect is shown by the dye Methylene Blue [542,543]. The concentration of H_2O is determined from the decrease in the colour of the Karl Fischer reagent after passage of the moist gas through the reagent [544].

The oxidising properties of $K_2Cr_2O_7$ are used to determine water in various biological materials [545]. The intensity of the colour of the reduced form of chromium depends on the water concentration. Using a scale of standards, it is possible to determine moisture using anhydrous copper sulphate [546,547].

Ether and ketones saturated with anhydrous LiCl acquire the orange-red colour characteristic of $LiCuCl_3$ in the presence of H_2O and copper perchlorate [548]. Moisture can alter the colour of solutions of chloranilic acid [549], hexanitrobenzene [550], complexes of diethylaluminium hydride with isoquinoline [551], and an acetone solution of anhydrous copper chloride [536].

Water in gaseous nitrogen can be determined by vacuum spectrophotometry in the ultraviolet range [552].

Various reagents ($SiCl_4$ [553] and $TiCl_4$ [554]) in contact with water-containing solvents form stable suspensions of hydrolysis products, whose light absorption depends on the moisture content.

The moisture content of monomers is determined by measuring the optical density of specimens cooled to −50°. The turbidity is proportional to the water content [555]. The turbidity at a CH_3COOH–toluene interface can be used to determine the concentration of moisture in the acid [556].

The turbidimetric method is used to determine water in methyl and ethyl thiols [557] and in fuels for aviation turbines [558]. The moisture content of gas is measured from the light extinction of the aerosol formed by passing the moist gas through oleum [559]. Water in liquid hydrocarbons [554] and motor fuel [560] can be determined nephelometrically.

Infrared spectroscopy can be used to determine water in gases, liquids, and solids over a wide range of water concentrations. The choice of analytical absorption band is determined by the chemical composition of the substance being analysed and the concentration of water being determined. At high concentrations of water (fractions of one percent and above) the bands in the range 5100–5300 cm^{-1} and 7100–6200 cm^{-1} due to the overtones and combination

frequencies of the stretching and bending vibrations of the HO groups of the water molecules are used[20,561-574]. The weak absorption bands at 1550–1650 cm^{-1} and 3590–3710 cm^{-1} due to the symmetric bending and asymmetric stretching vibrations of the HOH and HO groups are used to determine traces of water[575-582].

Infrared spectroscopy is widely used to determine water in various organic liquids: alcohols[561,575,577,582-585], glycols[561,582], dioxan[561,582,586,587], ketones[573,575,577,582,583,586,588], 1,1-dimethylhydrazine, diethylenetriamine, monomethylhydrazine[562,563,589], glycerol[565,583], esters[573], aldehydes[580], benzene, toluene, xylene[590], CCl_4[586,587,590,591], chloroform[582,586,587], ethyl bromide[589], homologues of pyridine[592], aniline[582,586,587], tetrabutyl phthalate[578], tetrahydrofuran[587], tributyl phosphate[593], dimethyldioxan[581], freon-22 refrigerant[594], organic solvents[585-599], and lubricating oils[600]. The limits of sensitivity of the determination of water in non-associated solvents and the relationship between the limits of sensitivity and the transmission coefficient of the background have been examined[590].

The methods of molecular spectroscopy are extremely effective and make it possible not only to determine the concentration of water in organic solvents but also to obtain considerable information on its state in solution, the bonds formed with the solvent molecules, and processes of hydration and extraction[20,601].

Special procedures are required for the determination of water in strongly corrosive inorganic liquids. Thus in the determination of water in liquid sulphur dioxide the NaCl or KCl cells are fitted with polyethylene and lead linings[576]. The conditions for the determination of water in liquid bromine[579,602] and fuming nitric acid[571] have been examined in detail.

Alkali metal halide discs, suspensions in Nujol, or solutions in D_2O have been proposed for the analysis of salts[568]. Methods have been developed for the determination of water of crystallisation[564,566,570,595,603], and water in carbohydrates[604] and milk fat[605].

In the analysis of vegetable materials by infrared spectroscopy the water is extracted beforehand with methanol[606], and in the analysis of coffee the water is separated by azeotropic distillation with dioxan[113]. The determination of water in complex minerals[607], silicates[568], silica gel[574], polymers[608], elastomers[609], films[569,596], and aluminium acetylsalicylate[610] has been described.

Infrared spectroscopy is sometimes used to analyse the products of the reaction of water with various reagents—2,2-dimethoxypropane[595] (acetone and CH_3OH are formed) and CaC_2, which liberates acetylene[609,611]. Various forms of apparatus have been described[12,83,571,583,584,595,608,609].

Infrared hygrometers for measuring the moisture content of air have been described[612,613]. The conditions for the analysis of gases at elevated temperatures and pressures have been examined[614].

6. NMR Spectroscopy. Nuclear magnetic resonance (NMR) can be used to measure the moisture content of liquids and solids. The determination of the moisture content of solid, loose, and fibrous materials is based on the fact that the water molecules are relatively mobile compared with the molecules of the main hydrogen-containing substance, so that the proton absorption curve obtained on a low-resolution instrument has the form of a very broad signal, on which the narrow line from the protons of water is superimposed[615,616]. At a concentration of water greater than 10%, the amplitude of the signal is linearly dependent on the moisture content[617-619]. At lower water concentrations, the bonding between its molecules and the adsorbent changes, and the dependence of the amplitude of the signal on the water concentration becomes more complex. In such instances, a calibration curve is used. Various instruments have been described[12,620-624].

The determination of water by the EPR method in wood, cellulose, fruit, starch[618,619,625-627], pectin[618], nylon[628], various granulated materials[619], peat[629], corn syrup and chewing gum[630], and a moving stream of coal[631] has been described. Small concentrations of water can be measured by determining the width of the absorption line[618]. The relaxation times have been used to determine the concentration of water in hardened epoxide resins and polyamides[632].

High-resolution NMR spectroscopy can be used to determine H_2O in acetone[633] and other liquids[634]. The dependence of the magnitude of the chemical shift of the protons of the water on its concentration can be used to determine water in, for example, CH_3CN, piperidine[635], and tributyl phosphate[636].

The NMR method is effective in the study of the sorption of water on various materials. It makes it possible to measure moisture contents over a wide range, rapidly, accurately, and without decomposition of the specimens. The control of technological processes from moisture content measurements is possible[621,622,637].

7. The Chromatographic Method. The chromatographic determination of water can be carried out either by direct separation of a mixture or by chromatographic study of the products of the previous reaction of appropriate reagents with water. The first version is carried out by the gas-liquid method, which is used to analyse mixtures with high water content. The liquid phase may consist of polyethylene glycol on refractory brick[638], Teflon[639,643], or porous glass[644], stearic or 12-hydroxystearic acids[645], and diiso-octyl phthalate on teflon[646], and tetrahydroxyethylenediamine on chromosorb[562]. The following reagents have been recommended for the determination of water by the second method: CaC_2[151,639,647-651], $LiAlH_4$[652], $NaAlH_4$[653,654], CaH_2[639,647,655], organic isocyanates[647], 2,2-dimethoxypropane[656,659], and lead tetra-acetate[660]. The gases formed and the organic liquids are analysed by absorption or gas-liquid chromatography.

The determination of water in the following materials has been described: butane[638], alcohols[661], mixtures of NH_3 and amines and mixtures of ethanol and butanol and ammonium carbonate[640], methanol, ethanol, CH_3COOH[641], pyridine[641,662], aliphatic acids[645], hydrocarbons[151,652,646], gases[654,663], hydrazine, monomethylhydrazine, 1,1-dimethylhydrazine, diethylenetriamine, and their mixtures[562,664], mixtures of the gases H_2, O_2, N_2, CH_4, and CO[651], pharmaceutical products[665], liquid alkenes, diene monomers, and various oxygen-containing compounds[653,666], sodium acetate and copper sulphate (with preliminary extraction of the water by methanol)[624], CH_3OH–aldehyde mixtures[644,650], the products of the manufacture of C_6H_5OH from isopropylbenzene[667], fruit[668], and water in the moon's crust[669].

Water in gases and hygroscopic liquids can be determined by reverse chromatography: a moist carrier gas with a water concentration greater than that of the substance being analysed is used, so that negative peaks appear on the gas chromatogram[670].

8. Other Methods. When a beam of β- or γ-radiation is passed through a material of uniform density,

a decrease in the intensity of the radiation beam is observed, depending on the moisture content. This phenomenon is used for the quantitative determination of the moisture content of soils, building materials and other loose materials, asphalt, wood[671,672], textiles[673], and petroleum[674]. A portable instrument for this purpose has been described[675].

A new method has been proposed for the determination of water in methanol[676] using kryptonates. In the presence of water, ^{85}Kr is liberated, and this is removed by a stream of nitrogen into a counting chamber and determined quantitatively.

Methods have been described for the determination of water by the third-component method using a radioactive substance in crystal hydrates[677,678], pharmaceutical products[679], sesame oil[680], silica gel, and iron ores[678]. The concentration of water in synthetic pigments and biopolymers can be determined by mass-spectrometric measurements after deuterium exchange[681].

A method for the determination of moisture has been based on the ability of hydrogen atoms to weaken a beam of fast neutrons[10,671]. The results of the measurements are little influenced by the salt content and density of the material and are not influenced by temperature and the moisture distribution. The use of the neutron method to measure the moisture content of lime raw materials[682], concrete[683,684], soil[684], wood, sand, moist salts[685,686], and lamp black[687] has been described. The development of a neutron moisture meter whose operation does not depend on the density of the material has been described[688-690].

The use of an ultrasonic method for the determination of small quantities of water in CH_3OH has been proposed[691].

It has been suggested that very small quantities of water can be determined by hygrophotography. An illuminated light-sensitive plate (a double complex of mercury and silver iodide) can undergo a restoration of colour with time. Moisture increases the rate of this process, and this makes possible the quantitative and qualitative determination of water in alcohols, medical products, soil, etc.[692-697].

A number of papers[698-700] and a draft standard[701] have been published on the determination of the moisture content of petroleum products and reactive fuel by centrifuging. Glass-fibre filters have been recommended for the determination of H_2O in sludges[702].

The absorption of radiowaves in the centimetre range by water has been made the basis of a method for the determination of moisture in polymers[703], foodstuffs[704,705], clay, sand, coal, tobacco, fertilisers, and oil[705]. Various moisture meters have been described[704-706].

The determination of water from the extinction of the luminescence of 4-chloro-2-sulphobenzalacetophenone in hydrocarbons has been described[707,708].

The thermal characteristics of the medium can be used as criteria for the determination of moisture in capillary-porous[709,710], dispersed, and fibrous[711] materials, magnesium perchlorate[712], sulphuric acid[713], fluorocarbons[714], and unsaturated hydrocarbons[715].

A review of methods for the determination of water by physical and physicochemical methods shows that these methods extend considerably the possibilities for the control and automation of production, are extremely rapid, and also extremely effective in the study of the state of water in substances in different states of aggregation.

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Mendeleev Institute of
Chemical Technology, Moscow.

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Organic Compounds in the Solar System

B.Yu.Levin

Information about the presence of organic and carbon-containing compounds in planets and their atmospheres, in comets, and in meteorites is reviewed. Data on organic compounds present in meteorites are the most important. Numerous studies on such compounds in recent years have led to a significant advance in our knowledge about their nature. In particular, "primary" organic compounds preserved within mineral grains have been detected. These proved to be the compounds which should have been formed in maximum amounts under quasi-equilibrium conditions in the system carbon-hydrogen-oxygen. This finding is based on both theoretical and experimental data. The data concerning the presence of organic compounds in the protoplanetary cloud are used to assess the possible history of these compounds on earth. The bibliography incorporates 108 references.

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1. INTRODUCTION

The existence of organic compounds in the solar system is one of the most important problems of cosmochemistry, since it is most closely related to the problem of the origin of life on earth and the formation of petroleum deposits on the latter. Modern data indicate not only a wide distribution of organic compounds in most of the bodies of the solar system but also the fact that these compounds may have entered into the composition of our earth in great abundance during its formation.

For a long time panplanetary cosmogony was ruled by hypotheses according to which the earth and other planets were formed from incandescent gaseous nuclei. At a temperature of several thousands of degrees organic compounds cannot exist and therefore these hypotheses led to postulates that organic compounds were produced on the previously formed earth after it had cooled sufficiently. Following Mendeleev, the formation of methane as a result of the action of hot steam on metal carbides was regarded as the beginning of this process.

During the last twenty years a radical change in the hypotheses concerning the "initial" state of planetary matter took place in planetary cosmogony: all modern cosmogonic hypotheses postulate the aggregation of planets from a cold gas-dust cloud surrounding the sun at one time. Organic compounds must also have been present in this cloud. Furthermore, in most recent investigations it was shown that various organic compounds, including some which were extremely complex, were present in the protoplanetary cloud at concentrations virtually corresponding to thermodynamic equilibrium.

Since carbon-containing compounds are an essential component of the "raw material" from which organic compounds are formed, the problem of the presence of these in various bodies of the solar system will also be touched upon.

2. ORGANIC COMPOUNDS IN PLANETS

The simplest carbon compounds enter into the composition of all planetary atmospheres when these exist at all. Such compounds are detected spectroscopically. The amount of a particular gas in the atmosphere can be estimated, if only approximately, from the intensities of the absorption bands. Usually the amount is expressed in terms of the thickness of a homogeneous layer of gas at standard temperature and pressure (s.t.p.). For gases with absorption bands in parts of the spectrum accessible to measurement and which are possible components of the planetary atmosphere, the absence of appreciable bands in the spectrograms of the planet permits the determination of the upper limit to the content of the gas in the atmosphere. Frequently this upper limit has been significantly reduced as apparatus was improved.

Spectroscopic data on the composition of planetary atmospheres serve as the initial basis for theoretical calculations of thermodynamic equilibrium in a mixture of gases of this kind and for the determination of the possible concentrations of other more complex molecules.

The hypotheses concerning the presence of carbon compounds, including organic compounds, within the planets themselves are based on indirect considerations. For the giant planets and their satellites, calculations involving models of their internal structure are based on data concerning their average density and on the equations of state for various substances, indicating an appreciable content of light compounds, among which the most important are organic and related compounds. The hypotheses concerning the presence of organic compounds within the planets of the earth group are based on considerations associated with the history of their development.

Spectroscopic observations show that the atmospheres of the giant planets Jupiter, Saturn, Uranus, and Neptune contain much methane and the atmospheres of the first two also contain ammonia. The amounts of these gases above the cloud level forming the visible surface of these planets are listed in Table 1. The increase of the amount of methane on going from Jupiter to Neptune is due to a change in the structure of the atmosphere associated with the reduction of temperature. The absence of ammonia from the atmospheres of Uranus and Neptune is accounted for by its freezing at the lower temperature of the cloud layer in these planets.

Hydrogen, which constitutes the main or at any rate an important component of these atmospheres, has scarcely any spectroscopic effect. Therefore our knowledge about its content above the cloud layer is poor even for Jupiter. Errors in the determination of the equivalent width of the quadrupole band lines of molecular hydrogen in the Jupiter spectrum are such that, even after new laboratory studies of these lines, the amounts of hydrogen found above the cloud layer of Jupiter vary from 30 to 200 km† [3,4]. The models of the part of the Jupiter atmosphere above the cloud level differ correspondingly [4,5]. In their spectroscopic observations of Jupiter, Spinrad and Trafton [4] did not observe absorption bands due to CH_2, NH_2, O_2, HNO, HDO, HCN, C_2H_2, HCO, and H_2O, but they do not quote data concerning the upper limits to their contents. Owen [6] compared the Jupiter spectrum in the near infrared with the laboratory spectra of a number of molecules and obtained the upper limits to their contents, which are listed in Table 2.

Table 1. Composition (cm at s.t.p.) of the atmospheres of the giant planets above the cloud level from spectroscopic data [1,2].

Gas	Jupiter	Saturn	Uranus	Neptune
CH_4	15 000	35 000	~350 000	~600 000
NH_3	700	<250		
O_2		<0.1	<0.1	
SO_2		<0.01	<0.01	

The occasional appearance of a red-brown colour of certain features of Jupiter (in particular the so called red spot) has been attributed from the beginning of the 1950's to the formation in the atmosphere of various organic molecules [7-11]. Urey [7] quotes as an example the following possible compounds: yellow diazomethane (CH_2N_2), red tetrazine ($C_2H_2N_2$), yellow azomethane [$(CH_3)_2N_2$], and yellow cuprene [$(C_2H_2)_x$]. However, it did not prove possible to obtain direct spectroscopic evidence for the presence of particular organic molecules on Jupiter.

In laboratory experiments, where a corona discharge was created in a simulated Jupiter atmosphere [12], the formation of the following molecules was observed: HCN, CH_3CH, C_2H_2, C_2H_4, and C_2H_6. In other experiments [13], where the simulated Jupiter atmosphere was subjected to hard ultraviolet irradiation (λ = 584 Å), the formation of methane, ethylene, and propane was observed. Saslaw and Wildey [13] also discussed theoretical chemical models of the upper Jupiter atmosphere postulating various chains of reactions between hydrocarbon molecules and ions. The equilibrium concentrations of a number of molecules in the upper layers of the Jupiter atmosphere, calculated on various assumptions concerning their temperature, are listed by Lippincott et al. [11]

Despite the enormous pressure, amounting to millions and tens of millions of atmospheres, in their interior, the giant planets have a low average density (0.7–2.2 g cm^{-3}). Calculations of the internal structure of these planets show that Jupiter contains about 80% of hydrogen and Saturn about 60%, the remainder of the mass of these planets being made up of helium, rocky materials, and also various light compounds such as methane, ammonia, carbon dioxide, water, and others. The average densities of Uranus and Neptune show that these planets contain little hydrogen and consist almost entirely of light compounds such as methane, ammonia, carbon dioxide, and others (with an admixture of rocky materials). When account is taken of the enormous mass of the giant planets, it is found that the overall mass of the light compounds which they contain, including organic compounds, is dozens of times greater than the mass of the earth. There is no doubt that these organic compounds are of a abiogenic origin.

† According to Owen's new determination [18], the amount of hydrogen is 85 ± 15 km.

Table 2. Upper limits to the contents of certain gases in Jupiter's atmosphere above the cloud level from spectroscopic data [6].

Gas	Upper limit to content, cm at s.t.p.
CH_3NH_2	800
C_2H_4	200
C_2H_6	250
SiH_4	2000
CH_3D	3000
HD	50000

The abundance of light compounds in the giant planets is associated with the abundance in the universe of the chemical elements which enter into the composition of these light substances. The most abundant element in the universe is hydrogen (60 wt.%, i.e. about 86% in terms of the number of atoms); the second place is occupied by the chemically inert helium (38 wt.% or about 14% in terms of the number of atoms). Next we have carbon, nitrogen, and oxygen, constituting altogether about 1.2 wt.% or 0.1% in terms of the number of atoms. The total number of atoms of all the remaining chemical elements taken together is only 0.8%. When gas with the cosmic composition (or a composition close to the latter) comes under the influence of fairly low temperatures permitting the formation of molecules, hydrogen molecules (H_2) are formed in the greatest amount, in the second place are compounds of hydrogen with C, N, and O atoms, such as methane, ammonia, and water, and finally in the third place there are compounds of carbon, nitrogen, and oxygen with one another, such as carbon monoxide, carbon dioxide, and CN. Thus the total cosmic abundance of chemical elements predetermines the abundance of carbon-containing and in particular organic compounds in cold cosmic bodies, whose matter has not been subjected to pronounced fractionation.

Organic compounds probably enter into the composition not only of the giant planets but also of their satellites. Unfortunately the average densities are known, if only approximately, for only five of the largest satellites of the giant planets (the four Galilean satellites of Jupiter and Titan—the largest satellite of Saturn), from which an indirect assessment of their composition may be made. The two satellites closest to Jupiter have a rocky composition and the two more distant ones (among the Galilean satellites) and Titan consist of 50% of rocky material and of 50% of light substances. These light substances probably include various organic compounds. An indirect indication

of this may be the presence on Titan of a methane atmosphere (possibly containing also ammonia) discovered by Kuiper in 1944.

We shall now consider the planets of the earth group. As early as the 1930's, the infrared spectrum of Venus revealed absorption bands which proved to belong to the carbon dioxide molecule. The amount of carbon dioxide present above the cloud layer forming the visible surface of Venus corresponds to a layer about 2 km thick (at s.t.p.). Kuiper, using spectroscopic data, found the upper limits to the possible contents of a number of other gases (Table 3).

Table 3. Composition of the atmosphere of Venus above the cloud level from spectroscopic data[1,14].

Gas	Amount, cm at s.t.p.
CO_2	200 000
CO	<3
N_2O	<100
CH_4	<20
C_2H_4	<3
C_2H_6	<1
NH_3	<4

Until recently the thickness and composition of the atmosphere under the cloud layer were unknown. In October 1967 the remarkable landing on Venus of the Soviet automatic station Venus-4 established that the carbon dioxide content is 90 ± 10%.[15]

Assuming a considerable concentration of water vapour in the atmosphere of Venus, Wildt put forward the hypothesis that the cloud layer of this planet consists of condensates of formaldehyde and its polymers. However, subsequently this hypothesis was abandoned. In the first place the attempts undertaken by Wildt himself to find the formaldehyde band in the ultraviolet part of the spectrum were unsuccessful. In the second place the water vapour content proved to be very small: in all several tens of grammes per cm^2. At present it is believed that the clouds most probably consist of crystals of ordinary ice.

At one time it was suggested that the entire surface of Venus is covered by a continuous ocean preventing the formation of carbonate rocks from the carbon dioxide atmosphere. Whipple and Menzell put forward the hypothesis of a soda water ocean, i.e. water saturated with carbon dioxide. Hoyle, believing that many organic compounds must have formed even in the protoplanetary gas–dust cloud under the action of various types of hard solar radiation, suggested the possibility of the existence of a petroleum ocean evolved from the inner parts of Venus. Both these hypotheses were rejected when several years ago radioastronomical measurements of the intrinsic thermal radio emission from Venus showed that its temperature is about 600°K. However certain investigators suggested that this temperature does not refer to the surface but the upper ionosphere of Venus. However, measurements by the automatic station Venus-4 showed that the temperature increases on going deeper into the atmosphere, reaching more than 500°K at the surface.

Since at the high temperature of the Venus atmosphere thermochemical equilibrium must be established rapidly, Mueller[16] estimated the possible content in this atmosphere of various hydrocarbons and found that it must be negligibly small. Recently this was confirmed by new more complete calculations‡ [11,17].

Studies of the spectrum of Mars for a long time failed to yield any information about the composition of its atmosphere. It was not until 1947 that weak carbon dioxide bands were observed in the infrared part of the spectrum. According to the latest data[18], the amount of carbon dioxide in the Mars atmosphere corresponds to a layer 75 ± 15 m thick (at s.t.p.). Spectroscopic estimates of the upper limits to the possible contents of other gases are listed in Table 4. Until recently it was believed that the atmosphere of Mars is thinner by a factor of 10 than the earth atmosphere and under such circumstances carbon dioxide would constitute less than 10 wt.%. The main component was believed to be molecular nitrogen, which is not revealed in the part of the spectrum accessible to observations. However, during recent years the application of new methods of observation resulted in a lower estimate of the density of the Martian atmosphere and a corresponding increase in the importance of carbon dioxide. Finally, in 1965 studies carried out with the aid of the American automatic station Mariner-4 showed that the Martian atmosphere is thinner than the earth atmosphere by a factor of 100 and therefore carbon dioxide constitutes not less than 50% and possibly the entire 100% of the atmosphere.

Table 4. Composition of the Martian atmosphere from spectroscopic data[19].

Gas	Amount, cm at s.t.p.	Gas	Amount, cm at s.t.p.
CO_2*	4500±2500	NH_3	<0,1
H_2O**	$(14\pm7)\cdot10^{-4}$	NO_2	$<1\cdot10^{-3}$
O_2	<2	N_2O	<0.08
O_3	$<4\cdot10^{-4}$	NO	<20
CH_3CHO	$<6\cdot10^{-3}$	H_2S	<7.5
CO	<1	H_2CO	<0.3
CH_4	<0.1	COS	<0.2

*According to Owen's new data[18], the amount of carbon dioxide is 7500 ± 1500 cm.
**Precipitated water. The amount varies both in space and in time.

The problem of the presence of an atmosphere on the planet Mercury, which is closest to the sun, remains to a large extent obscure. Polarimetric observations indicated the existence of an atmosphere with a mass of 3 g cm^{-2} (on earth about 1000 g cm^{-2}), but there was no spectroscopic confirmation of its existence. In 1963 V. I. Moroz observed a slight increase in the intensity of the carbon dioxide bands in the infrared spectrum of Mercury relative to that of the moon (in the latter case the carbon dioxide bands are due to the presence of carbon dioxide in the terrestrial atmosphere).

For a long time it was believed that one side of Mercury is always turned towards the sun and therefore it might have been supposed that in the night hemisphere of the

‡ In all these calculations models of the Venus atmosphere postulating an unduly high pressure at the surface and an unduly high nitrogen content were employed. However, the conclusion concerning the negligibly low concentration of hydrocarbons is almost independent of these initial data and remains valid also for the true atmosphere of this planet.

planet, under the conditions of a constant low temperature, there are frozen volatile substances. However, radar observations showed that Mercury rotates about its axis with a period amounting to two thirds of its period of rotation about the sun. In agreement with this finding, radio-astronomical observations, permitting an estimate of the surface temperature to a depth of several meters, do not reveal an appreciable difference between the day and night hemispheres. Thus the possibility of the existence of frozen volatile substances is completely excluded for the major part of the surface of Mercury, with the possible exception of the polar regions whose temperature remains unknown.

We have no information about the presence of organic compounds on the moon, which lacks an atmosphere. Only theoretical considerations concerning their possible presence have been put forward. Thus Sagan[20], believing that a reducing atmosphere consisting mainly of methane, ammonia, and water existed at one time on the moon, put forward the hypothesis that organic substances formed in this atmosphere under the action of solar ultraviolet radiation may have persisted in the upper layer of the moon. In an atmosphere with this composition fairly complex organic molecules with molecular weights up to 100 are formed under the action of ultraviolet radiation (and electric discharges): amino-acids and other organic acids, pyrroles, pyridines, and simple hydrocarbons and their polymers (see, for example, Miller[21] and Miller and Urey[22]). According to Sagan's estimate, the amount of amino-acids with a molecular weight of about 100 alone, formed during ten million years in an atmosphere opaque to ultraviolet rays, may be of the order of 5 g cm^{-2} (for a quantum yield of 10^{-6}). The heavy molecules produced must have sunk towards the surface and then on to the surface itself where they were protected by the atmosphere from the destructive short-wavelength radiation. As the atmosphere became dissipated, ultraviolet radiation must have partially decomposed the organic molecules, while some may have been converted into more complex compounds (for example, polypeptides may have been formed from the amino-acids). Sagan believes that organic compounds on the moon were protected from complete degradation under a layer of meteoritic material and have persisted up to the present time on the elevated "mainland" parts of the lunar surface, while in the sections corresponding to the "seas" they were destroyed by the lava flow.

However, the picture drawn by Sagan is probably incorrect for a number of reasons. Firstly, recently serious doubts have been expressed concerning the hypothesis that the primary atmospheres of earth type planets and the moon consisted mainly of methane, ammonia, and water. Data on the oxidation equilibrium between gases and silicate melts showed that, for the evolution of methane to occur, the melts must have contained metallic iron, which is in fact not the case. Gases of the same composition as those evolved from volcanos[23] must have been evolved from the basalt magmas. Consequently the lunar atmosphere must have consisted of water, carbon dioxide, sulphur dioxide, molecular hydrogen, and carbon monoxide. Secondly, the density of the atmosphere at the surface of the moon can have scarcely exceeded one millionth part of the density of the present day terrestrial atmosphere at the surface[24], i.e. was the same as the density of the terrestrial atmosphere at the height of about 150 km. This density is altogether too low both for the formation of a sufficient number of organic molecules and for their protection from solar ultraviolet radiation after they have sunk to the lunar surface. Thirdly, impacts of meteorites of various dimensions keep "ploughing up" the surface layer of the moon to a depth of several metres and therefore favourable conditions for the protection of organic matter do not exist there.

Gilvarry[25,26] goes much further than Sagan and suggests that biogenic organic substances may be present on the moon. He is the only astronomer who suggests that real seas, in which even life may have existed, were present at one time on the moon. Gilvarry starts from the unlikely hypothesis of extremely rapid evolution of water from the interior of the moon and greatly overestimates the possible duration of its persistence on the lunar surface. This hypothesis has not found any supporters.

There exists, however, another theoretical possibility of the presence on the moon of considerable amounts of organic compounds, including hydrocarbons. It is associated with the presence of these substances in meteorites (see section 4) and, judging from all available data, in the materials from which earth type planets and the moon aggregated. As noted by Wilson[27], if the average hydrocarbon content in meteorites (about 0.01%) is assumed for the primary material of the earth and the moon and account is taken of the fact that only part of these may have been converted into liquid hydrocarbons by cracking in the interior parts of these bodies, then the amount is still sufficient to account for the origin of all petroleum accumulations on earth. Wilson put forward the hypothesis that the lunar seas are covered by the asphalt remaining after the evaporation of lighter hydrocarbons which emerged in the form of petroleum from the interior of the moon. Wilson's hypothesis was objected to by Mueller, who is a supporter of the biogenic hypothesis of the origin of petroleum. However, Wilson's quantitative estimates are quite correct. Nevertheless there is a serious astronomical basis to doubts concerning the possibility of such large petroleum outflow on the surface of the moon.

As a result of the extremely low thermal conductivity of the surface layer of the moon, the daily temperature variation penetrates only to a depth of about 0.5 m; at greater depths the temperature remains always constant. In the equatorial zone this constant subsurface temperature is about −30°C and in the polar regions it is considerably lower. As a result of the constant increase of temperature with depth, a temperature of 0°C is attained at a depth of 2–4 km in the equatorial zone and at a depth of 15–20 km in the polar regions. The existence of a layer of subzero temperatures implies the great probability of the existence of a layer of permafrost. In the polar regions of the moon not only water vapour arising from the interior but also carbon dioxide can freeze in this layer. The permafrost layer must prevent the outflow on to the lunar surface of non-biogenic "petroleum" and in general the evolution and dissipation of volatile organic compounds; their presence in large amounts in the interior layers of the moon appears very likely. However, the properties of the lunar surface, its dielectric constant and low reflectivity, have been successfully explained by astronomers on the basis of the silicate nature of its composition without resorting, like Wilson[27], to the asphalt or petroleum coke hypothesis.

It should be added that under the layer of subzero temperatures there must exist a fairly thick layer in which water may exist in the liquid state. The permafrost layer (if it does exist on the moon) is self-sealing, i.e. all cracks in it are rapidly eliminated. A coating is obtained which does not permit the escape to the outside even of gases and therefore it allows the existence of a kind of "internal atmosphere"[28]. The only case of the evolution of gases from the interior of the moon was observed by Kozyrev in 1959. In one of the spectrograms of the moon which he obtained

there is an emission band extremely similar to the most intense C_2 band which is also observed in the spectra of comets.

All that has been said above concerning the possibility of the existence on the moon of a permafrost layer, containing and retaining organic compounds, applies to a considerable extent also to Mars.

3. ORGANIC COMPOUNDS IN COMETS

Apart from the giant planets, the solar system contains yet another type of bodies consisting mainly of volatile materials, namely comets. The solid nuclei of the comets are small, usually between several hundred metres and several tens of kilometres in diameter and consist of "ice" comprising different gases with an admixture of involatile rocky materials (10–30 wt.%). In their structure the comet nuclei must resemble enormous lumps of snow (however, these are black and not white) rather than blocks of ice. They move around the sun along extended orbits and most of the time they remain far from it. The temperature of the nucleus is then extremely low and therefore gases are not evolved from the latter. On approach to the sun, the surface layers of the nucleus are beginning to heat up and the evolved gases form an atmosphere which is continually dissipated—the head of the comet and the tail.

Spectroscopic observations on the heads and tails of comets reveal the presence of C_2, C_3, CN, CH, OH, NH, NH_2, CO, and N_2. Until recently it was believed that all these chemically unstable radicals are generated as a result of the photodissociation of chemically unstable parent molecules evolved (desorbed) from the comet nuclei. Methane, ammonia, carbon dioxide, and water were postulated in the first place as parent molecules of this kind. However, the problem of the parent molecules is much more complex.

Donn and Urey[29] put forward the hypothesis of the presence in the comet nuclei of considerable amounts of frozen unsaturated radicals. However, subsequently they changed their view. Even under laboratory conditions radicals are frozen only with considerable difficulty and under natural conditions they could enter into the composition of comet nuclei only in a small amount. Donn[30] estimated this amount as approximately 1%.

Delsemme and Swings[31,32] believe that the wide variety of volatilities of the hypothetical parent molecules enumerated above is incompatible with the results of observations on comets, which indicate that the ratio of the amounts of different molecules varies little with the distance of the comet from the sun, i.e. with the temperature of the surface of the nucleus. Therefore they suggest that the molecules in the comet nuclei are present in a hydrated form (such as $CH_4.6H_2O$), which gives rise to similar volatilities of all the compounds. Although their initial evidence appears unsound (the differences in volatility will be rapidly compensated during evaporation by the generation of various concentration gradients in the surface layer of the nucleus), the idea of an abundance of water in comet nuclei is probably valid. In recent years it was established that the lines due to atomic oxygen observed in the spectra of comets do not originate from the superposition of the luminescence of the terrestrial atmosphere but are due to the comets themselves. Oxygen atoms are produced as a result of the photodissociation of water.

The comet nuclei were formed at extremely low temperatures and therefore it may be suggested that initially they consisted of amorphous matter with a disordered arrangement of a wide variety of molecules, radicals, and atoms[33]. Subsequently the radioactive elements entering into the composition of the involatile fraction must have heated the central part of the nucleus to a temperature of about 50°K or above and must have caused the evaporation (sublimation) of the most volatile components and their diffusion through the porous material of the nucleus and condensation in the cold outer layers[34]. During this process the initial composition and structure of the material of the nucleus might have changed significantly.

Observations on some of the radicals contained in the comet atmospheres make it possible to establish the lifetimes of the parent molecules from the instant of their evolution from the comet nucleus to their photodissociation. In particular the lifetimes of molecules giving rise to C_2 and CN do not exceed 1–3 h at a distance of one astronomical unit from the sun.

Potter and Del-Duca[35] made laboratory measurements of the ultraviolet absorption cross-sections (in the region 4000–1300 Å) for ethylene, acetylene, methane, acetonitrile, monocyanoacetylene, dicyanoethylene, dicyanogen, methylamine, hydrazine, ammonia, hydrogen peroxide, and water, and using data on the ultraviolet emission intensity of the sun, found the lifetimes of these molecules in the interplanetary space. It was found that the lifetimes of molecules whose decomposition can give rise to C_2 and CN amount to tens and hundreds of hours at a distance of one astronomical unit from the sun, which is inconsistent with the astronomical data. Consequently C_2 and CN are formed by the photodissociation of some other uninvestigated molecules (for example, molecules, which are stable only at low temperatures) or they are formed not by photodissociation but as a result of another process, for example molecular collisions in the immediate vicinity of the nucleus.

Laboratory studies of Stief and De-Carlo[36] showed that, from the purely spectroscopic point of view, the parent molecule of C_2 may be acetylene (C_2H_2) or an acetylene molecule, but not ethylene or ethane. However, according to Potter and Del-Duca[35], acetylene must be excluded because its lifetime in the radiation field of the sun is much too great.

Stief and De-Carlo also found that NH observed in comets cannot form as a result of the photodissociation of ammonia (NH_3), but can be produced by the dissociation of hydrazine (N_2H_4) or some other related molecule.

Thus, although the presence of organic molecules in the nuclei of comets is not subject to doubt, only the first steps have been taken so far in the determination of their exact nature. A fairly complete idea about the organic compounds in the nuclei of comets will probably be derived in the next few years by direct analysis of the matter from the nuclei by means of automatic apparatus mounted on a space rocket which will be sent to intercept the comet.

4. ORGANIC COMPOUNDS IN METEORITES

The meteorites falling on earth are fragments of asteroids, i.e. bodies located at the boundary between the zone of the earth type planets and that of the giant planets. In the regions of the planetary system remote from the sun there exist probably objects of meteorite dimensions consisting of "ice" comprising different gases, i.e. similar to the nuclei of comets. However, bodies moving in the region of the earth orbit, i.e. in the vicinity of the sun, consist of refractory substances—silicates and iron–nickel alloy.

All meteorites contain at least a small amount of carbon and carbon compounds, including organic compounds. In particular, gases evolved when meteorites are heated contain carbon dioxide, carbon monoxide, methane, and ethane (together with molecular hydrogen, hydrogen sulphide, and sulphur dioxide). However, there exist chondrites of a rare type (about 30 are known) containing several per cent of organic compounds. These are known as carbonaceous chondrites. Carbonaceous chondrites contain carbon, predominantly in the form of high-molecular aromatic compounds and also in the form of bitumen-like material. In addition they contain hydrated minerals and free sulphur. The material of carbonaceous chondrites was never heated to temperatures in excess of 200–300°C. Mason's review[37] is specially devoted to carbonaceous chondrites.

Wiik[38] showed that carbonaceous chondrites can be naturally divided into three types, differing in the content of volatile substances and structure. The average carbon and water contents (expressed as percentages) are as follows:

	type I	type II	type III
C	3.5	2.5	0.5
H_2O	20.1	13.4	1.0

(The maximum observed carbon content is 4.83%).

Carbonaceous chondrites of type I have a composition very similar to that expected for a solid condensed in the protoplanetary cloud. Even the content of widely distributed elements is almost identical with the "cosmic" abundance, while in meteorites of other types there is a smaller or greater deficit. Carbonaceous chondrites contain large amounts of primary inert gases, i.e. gases captured from the surrounding medium in the formation of the meteorite material (and not evolved in consequence of radioactive breakdown). It is now believed that, of all the substances at present available to us, carbonaceous chondrites of type I are closest to the primary matter from which the planets of the earth type are formed.

The presence of organic compounds in carbonaceous chondrites was established as early as 1834 by Berzelius, who, however, found it difficult to identify them because of the complexity of their structure and the small amount available for analysis. In the XIXth century investigations consisted mainly in the isolation of organic compounds by sublimation or by extraction with solvents such as alcohol or petrol. The amount of bituminous substance isolated rarely exceeded 1% of the total weight of the specimen. However, the major part of the carbonaceous substance consists of a black carbon-like material which is not acted upon by solvents. It has been frequently called graphite or amorphous carbon. As early as 1864, however, Cloëz, who studied the meteorite Orgueil showed that this black substance is an organic complex. He isolated it by dissolving the inorganic component and obtained 6.4% of an insoluble residue. He assumed that this residue is a complex mixture of compounds with a high molecular weight. It is now known from X-ray diffraction data that the black substance in all carbonaceous chondrites is amorphous and consists of an aromatic polymer[39].

After a break of more than half a century, studies on the organic material in carbonaceous chondrites were resumed in the 1950's. Mueller[40] irradiated with ultraviolet light 20 carbonaceous chondrites and found that 19 of them do not fluoresce. Hence he concluded that they do not contain free hydrocarbons with an atomic ratio $H:C > 1.4$. However, further studies showed that luminescent extracts can be obtained from all carbonaceous chondrites. Mueller extracted organic compounds from the Cold Bokkeveldt meteorite by means of organic solvents. The substance extracted after the removal of sulphur crystals (10–12%) proved to have the following composition: C 19.8%; H 6.7%; N 3.2%; S 7.2%; Cl 4.8%; O and other elements 40.0%; ash 18.3%; the presence of chlorine is interesting. In contrast to solutions of terrestrial minerals of biological origin, which are always optically active, the solution of the extracts from the Cold Bokkeveldt meteorite showed no optical rotation within the limits of accuracy of the apparatus (0.02°). Mueller concluded that the organic substance from the meteorite consists of complex organic acids with different solubilities. They were produced by non-biological polymerisation in a gaseous medium containing nitrogen, sulphur, and chlorine. Judging from the difficulty of the dissolution of silicates, this substance envelops the strong particles.

Boato[41] studied the isotope composition of carbon and hydrogen from 12 carbonaceous chondrites and found appreciable differences between individual meteorites and in certain cases also between different parts of the meteorite. This is the result of fractionation processes or chemical reactions in the early stages of the formation of the meteorite.

At the beginning of the 1960's Calvin[42] and Briggs[43] showed that organic substances can be extracted from carbonaceous chondrites not only with organic solvents but also with water. The infrared and ultraviolet spectra of the extracts from the Orgueil, Murray, and Alais meteorites investigated by Calvin showed that they contain a wide variety of organic compounds including hydrocarbons and heterocyclic bases. Cytosine was found in the extract from the Murray meteorite[42]. On the other hand, no amino-acids were found in the aqueous extracts. On the basis of the infrared and ultraviolet spectroscopic data and data obtained by paper chromatography, Briggs[44] suggested that the extracts from the Mokoia meteorite contain purine or the related imidazole compound and also conjugated cyclic systems. He attributed the solubility in water to the presence of polar groups, such as carboxy- and hydroxy-groups and amines. He also found no indication of the presence of amino-acids.

An enormous explosion of interests in carbonaceous chondrites was stimulated by the work of Nagy and coworkers published in 1961.[45,46] In the first of these Nagy, Meinschein, and Hennesy[45] present the results of mass-spectrometric analyses of the linear and cyclic hydrocarbons from the Orgueil meteorite. They investigated a number of fractions distilled at temperatures between 100° and 400°C. Having found a similarity in the positions of the maxima on the distribution curves with respect to the carbon number for various hydrocarbons from the meteorites and from substances of biological origin—oils and sea deposits—the authors regarded this as evidence for the occurrence of biological processes "outside the limits of the earth", i.e. in the parent bodies from which the meteorites were derived.

In the second paper Lakus and Nagy described the results of the microscopic study of the Orgueil and Ivuna meteorites. They assert that both meteorites contain an enormous amount of microscopic particles (about 10 μm) resembling fossil seaweed, pollen, or spores. They amount to thousands per milligramme. These particles, which have come to be called "organised elements", are dyed by biological stains. Referring to the previous paper, in which it was claimed that biochemical compounds were observed, the authors expressed the view that the "organised elements" are indeed petrified unicellular micro-organisms.

As pointed out correctly by Briggs[47], to establish the biological nature of the organic material from meteorites, "it is necessary to show that the composition of the mater-

ial is identical with that wihch can be obtained on breakdown of a terrestrial cellular life form. If the composition is different, it follows that the material is either of an abiogenic nature or that it originates from an extraterrestrial life form having a chemical composition different from that of the terrestrial life forms familiar to us. If this latter hypothesis is adopted, it is impossible to employ merely the presence of organic matter in meteorites as a criterion of extraterrestrial biogenic processes, since evidently one can say about any chemical substance that it is part of a completely unknown and hypothetically alien life form. The last consideration is important, since it is difficult to doubt that in many of their properties the meteoritic organic compounds do not resemble terrestrial biological residues".

As regards the "organised elements", the attempts to revive the micro-organisms from meteorites proved unsuccessful[48] and the investigations had to be based merely on their morphology which is a very indefinite and unreliable procedure.

The conclusions of Nagy, Meinschein, and Hennessy were objected to by Anders[49] on several counts, who emphasised that despite their captions, the mass spectra quoted by these workers for the range C_{15}–C_{30} do not refer to the pure hydrocarbons (straight-chain alkanes and mono-, di-, and tri-cycloalkanes), including also the degradation products of heavier molecules with masses up to 600. He noted that the curves for the oil and sea deposits differ appreciably from one another and therefore there is no standard curve characteristic of hydrocarbons of biological origin. Anders also pointed out a number of possibilities of contamination of the meteorite by terrestrial biogenic hydrocarbons: as a result of contact with the hands, the "respiration" of the porous meteorite during changes in atmospheric pressure, etc. He concluded his paper with the following words: "even if it should be possible to prove a close resemblance in the distribution of compounds, as opposed to cracking patterns, a logical difficulty remains: it must also be proved that a similar distribution could not have arisen in the solar nebula by purely inorganic reactions. Like all negative proof, this is impossible to obtain. A far more promising approach would be to look for optical activity in meteorite hydrocarbons. Optical activity is a universal and indispensable property of life as we know it and its discovery in meteorites would go a long way toward convincing sceptics such as myself of the onetime existence of life on the meteorite parent bodies".

It is therefore difficult to convince the investigators of meteorites of the possibility of the existence of life on their parent bodies, which would imply a complete revision of the modern hypotheses concerning the origin and history of these bodies. Nevertheless, as far as the astronomical and cosmochemical data are concerned, there is no justification for such revision.

The critical remarks of Anders were published together with the reply of Nagy, Meinschein, and Hennessy which they conclude with the hope that their further results would completely confirm their preliminary conclusions. In Urey's words[50], these authors were very surprised by the reaction to their paper from meteorite experts. They believed that they had made an interesting discovery which would be accepted without objection.

In 1962–1963 a vigorous controversy developed around the work of Nagy and coworkers. In March 1962 a series of articles were published in Nature (No. 4821) on this question (Urey; Briggs, and Kitto; Fitch, Schwarcz, and Anders; Bernal; Nagy, Klaus, and Hennessy). In May 1962 a special conference devoted to the "organised elements" was held in New York (for the conference report, see Urey[51]). A number of papers have been published both by the supporters of the biological origin of the particles discovered and by their opponents, who explain them away by the unusual forms of natural minerals or by contamination by terrestrial particles of biological origin—pollen, pores, etc.

Klaus and Nagy discovered several types of "organised elements". Fitch and Anders[52–54] divided these elements into two groups: particles with a very complex structure and particles with a much simpler structure. There is no doubt about the latter that they belong to the meteorite itself. However, Fitch and Anders and also Mueller[55,56] showed that the Orgueil and Ivuna meteorites contain microscopic hexagonal crystals of troilite (FeS), which resemble the hexagonal "organised elements" described by Klaus and Nagy. By centrifuging in heavy liquids the meteorites ground to a powder, as was also done by Klaus and Nagy to concentrate the "organised elements", Fitch and Anders also found spherical particles resembling the spherical "organised elements", but which they showed to be supercooled drops of sulphur and hydrocarbons. As regards the group of particles with complex morphology which resemble terrestrial micro-organisms both in structure and in the remaining properties, there are grounds for the belief that their presence in the Orgueil meteorite (probably only in a few individual lumps of the meteorite) is a result of contamination.

The experiments of Imshenetskii and Abyzov[57] showed that not only stone but also iron meteorites are completely permeable to soil micro-organisms. It is therefore not surprising that Roy found Johnstown achondrite to be contaminated with two types of terrestrial bacteria and Oro and Tornabene[58] isolated three types of terrestrial bacteria on the Murray and Mokoia carbonaceous meteorites. These meteorites were stored simply wrapped up in paper. A lump of the Orgueil meteorite, which these authors also investigated, was preserved in a museum in a sealed glass vessel and no contamination with micro-organisms could be observed. In all the remaining cases of the observation of bacteria in meteorites, it was asserted without sufficient evidence that bacteria brought by the meteorite from space had been revived. The contamination of meteorites by terrestrial bacteria results at the same time in contamination by terrestrial biogenic organic substances, which may be erroneously assumed to belong to the meteorites themselves§.

Both Briggs and Anders and Fitch noted that the attribution of a biological origin to the "organised elements" on the basis of morphological data is unconvincing, since it is based to a large extent on subjective assessments. Later Urey[50] in his review on the hypothetical presence of biogenic substances in meteorites¶ also wrote that "to a chem-

§ In one of the lumps of the Mokoia meteorite which was contaminated with pieces of wood, spores, and radiolaria after falling, Mueller[60] found a resinous substance which subsequent investigations showed to be identical in composition with the substance exuded from the root of the tree on which the meteorite had fallen.

¶ Urey's review has the unfortunate title "Biological Material in Meteorites", which creates the impression that the author firmly admits the biogenic nature of the organic compounds from meteorites. Recently Urey et al. published a special note[59], in which they emphasise that they do not regard the biogenic origin of these compounds as proved, but at the same time they find that there is no adequate proof for their abiogenic nature.

ist, morphological forms appear to be an unsatisfactory basis for identification of biological remains because so many artifacts of approximately the size of micro-organisms, can be made both from organic material and inorganic material". At the same time Urey noted that the evidence in favour of the presence of organic substances is such that if terrestrial objects and not meteorites were concerned there would be no question about their validity. In the case of meteorites, as pointed out both by himself and Anders and Fitch, further objective study of the factual data is essential.

It was indeed essential both because of the exceptional importance of the problem of the existence of extraterrestrial life and because it might reveal the weak points of the method used previously to establish the presence of life residues in terrestrial specimens. An extremely important step was taken in 1965 when Anders and coworkers succeeded in obtaining proof that the organic compounds found in meteorites might have arisen in the protoplanetary cloud without any participation of biological processes (see below). As regards the "organised elements", nowadays almost everyone admits that the part of these belonging to the meteorite itself is abiogenical in nature and consists of complex crystals and mineral grains or hydrocarbon droplets, while the remainder are a result of the contamination of the meteorite by earth spores, pollen, etc.

In 1962–1965 a series of studies on the organic material in carbonaceous chondrites was carried out by Vdovykin[61]. These investigations dealt both with the bitumen-like material extracted by solvents and with the high-molecular insoluble phase. Luminescence analysis of the extracts obtained by cold extraction with various solvents by Florovskaya's method revealed the presence in these materials of reducing, neutral, and acid organic compounds: oils, neutral and acid resins, and humic components. The content of oils was 45–75% and that of asphaltenes 9–20%. The study of the fluorescence band spectra established the presence of condensed aromatic hydrocarbons[62].

The high-molecular phase constituting more than 90% of the carbonaceous substance was investigated by X-ray diffraction, electron diffraction, and microdiffraction methods. This phase consists mainly of an amorphous organic substance in which crystalline polymers are encountered and also very small inclusions with some order in the arrangement of carbon atoms. A gradual transition of the high-molecular phase of the carbonaceous substance into carbon black, and subsequently to graphite was noted. This phase, consisting of highly condensed aromatic compounds, is present also in achondrites and in the graphite inclusions in iron meteorites.

During these years a large number of papers were also published abroad and their number continues to grow. These studies dealt with the aromatic and aliphatic compounds in the bitumen-like (extractable) and high-molecular phases of the carbonaceous substance and also with compounds containing sulphur, nitrogen, and the halogens. Hayes[63] reviewed systematically the work published in 1953–1966. Information about this work, including the bibliographical references, is also available in Vdovykin's book[61]. Many organic compounds have been observed with absolute certainty but for others there are discrepancies in the results.

An example of the pitfalls encountered in the analysis of organic compounds in meteorites is provided by the history of the detection of amino-acids in them. Thus Degens and coworkers reported the observation of sugars and amino-acids in a number of carbonaceous and ordinary chondrites[64,65]. On this basis, Degens[66] speaks of a genetic relation between the organic material from meteorites and from sea deposits.

However, Oro and Skews[67] soon detected the same amino-acids as those found in meteorites on the skin of human fingers and actually in similar relative amounts. It was found that the amounts of amino-acids detected in meteorites can be fully accounted for by the amino-acids present in the fingerprints remaining after the meteorites have been handled. Therefore Oro believes that his data support the results of Calvin[42] and Briggs[44], who failed to detect amino-acids in meteoritic organic materials (see also Ref. 68). Probably their detection in other investigations[64–66] can be accounted for by the contamination of the specimens studied.

A pitfall of another kind is clearly demonstrated by the study of the isotopic composition of hydrogen carbon, and sulphur from the organic material in four carbonaceous chondrites carried out by Briggs[68]. He observed enrichment in deuterium and sulphur-34 and depletion in carbon-13. As regards the enrichment in deuterium and depletion in carbon-13, this substance resembles terrestrial materials, but the enrichment in sulphur-34 is contrary to what is observed on earth. Therefore Briggs believes correctly that his results confirm the extraterrestrial origin of the substance which he investigated. However, if only hydrogen and carbon were studied, the opposite conclusion would probably have been arrived at!

The application of the ESR method led to the detection of free radicals in the carbonaceous material in meteorites[61,69,73]. It was found that the concentration of free radicals is 10^{16}–10^{17} per gramme of carbon. Repeated measurements after the irradiation of the meteorites with X-rays established that the free radicals are associated with aromatic structures. Soviet investigators attribute the formation of radicals to the effect of cosmic radiation. According to French scientists, the carbonaceous components of the meteorite material are at least partly of biological origin. However, Urey[50] in his discussion of this finding also pointed out that free radicals might have arisen in the abiogenic material of meteorites under the influence of the radiation to which they were subjected in the interplanetary space. Schulz and Elofson[73], who investigated the Orgueil meteorite, carbonised the carbonaceous material at different temperatures and concluded that this meteorite had never been subjected to a temperature in excess of 300°C. They note that the presence of free radicals can be explained in different ways and that an abiogenic origin is also possible.

The studies discussed above led to a significant advance of our knowledge about organic compounds in meteorites but did not and could not provide a definite answer to the question of their biogenic or abiogenic nature. At the same time experimental studies, begun even earlier, continued to reveal new possibilities in laboratory abiogenic synthesis[12,21,22,42,43,74–84].

Perhaps one of the main difficulties arises in connection with the explanation of the abiogenic origin of saturated hydrocarbons. In meteorites they are mainly of the unbranched type, although abiogenic synthesis usually yields a mixture of branched and unbranched compounds. At the same time saturated hydrocarbons in most terrestrial organisms are unbranched. Only Wilson[74] succeeded in obtaining by an abiogenic procedure similar high-molecular hydrocarbons on the surface of a salt solution by passing an electric discharge through a mixture of methane, ammonia, and hydrogen above the solution. It is also known that thin films of waxy material are formed in electron microscopes on surfaces subjected to the action of an electron beam.

Similar waxy coatings were observed on the surface of cosmic dust[85]; they probably consist of a hydrocarbon polymer formed in the interplanetary space under the action of radiation.

Vigorous controversy has developed on the question of the optical activity of the organic compounds from meteorites[86-90] (see also Refs. 61 and 63). The rotation of the plane of polarisation is extremely rarely observed in the products of non-biological laboratory processes, but is a characteristic feature of all substances of biological origin and therefore the detection of rotation in extracts from carbonaceous chondrites would be important evidence in favour of the biogenic nature of these extracts, but would still not constitute incontrovertible proof of this. Since the time when Mueller's work was carried out, the precision of measurements increased, but later observations also led to the conclusion that the extracts have no optical activity. The reported low optical activity in certain meteoritic extracts is probably associated with the surface contamination of the specimens by fingerprints.

An important stage in the investigation of the nature of the organic material in meteorites was reached with the work of Anders and his coworkers. These investigators succeeded in obtaining data on the composition of the organic compounds which were contained within the mineral grains and therefore had not lost their volatile components, in contrast to the remaining larger portion of organic material in the meteorite. The composition of this substance is similar to that observed for the equilibrium distribution in carbon-rich carbon–hydrogen–oxygen mixtures. Therefore Studier et al.[91] suggested that the organic substances present in meteorites were formed in the interplanetary cloud and were then captured on formation of the parent bodies from which the meteorites originated. Initially this concept was based on theoretical calculations of the equilibrium concentrations of various compounds in the system carbon–hydrogen–oxygen and was then supported by experiments.

The basic idea of their investigation was as follows. During the course of the last few millions of years of their existence, the meteorites were heated to 250–300°K each time they passed through the perihelion. Therefore the most volatile substances could persist only in a few "secluded" corners within the mineral grains, while the less volatile substances persisted also in the form of surface coatings and in the interstices between the grains. Carbonaceous chondrites contain traces of primary inert gases firmly retained within the mineral grains. These gases were captured from the primary gas phase (from the protoplanetary cloud or, in the view of certain investigators, from some atmosphere) during the formation of the carbonaceous chondrites or the minerals included in them. The above investigators made an attempt to elucidate whether other volatile substances were captured at the same time.

Volatile substances were evolved in a vacuum at low temperatures from freshly ground specimens of three carbonaceous chondrites. The fractions evolved at different temperatures (up to 140°C) were investigated using a mass-spectrometer, whereby mass spectra up to a mass number of 500 could be studied. The substances which could be identified on the basis of 28 individual analyses are listed in Table 5†.

The new measurements emphasised the predominance of aromatic hydrocarbons compared with aliphatic hydrocarbons. An important discovery was that the amount of ethane is smaller by a factor of at least 1000 than of methane. From the analysis of these results, the authors concluded that the volatile compounds which they detected do indeed represent little changed residues of the primary gaseous medium in which the carbonaceous chondrites were formed and on this basis they endeavoured to elucidate the origin of the organic compounds. Two alternative hypotheses are possible: (a) a non-equilibrium process associated with some high-energy source (for example Mueller–Urey reactions presupposing irradiation with ultraviolet light or charged particles), or (b) an equilibrium process presupposing reactions in the gaseous medium under conditions of thermodynamic equilibrium.

Table 5.*

Compound	Orgueil	Cold Bokkeveldt	Murray	Compound	Orgueil	Cold Bokkeveldt	Murray
H_2	++	+	++	$C_6H_4(CH_3)_2$	+E		
He			+	C_6H_5Cl	+		
CH_4	++	++	++	$C_6H_5C_2H_7$	+		
NH_3	–	–	–	$C_6H_5CH(CH_3)_2$	+		
H_2O	++	++	++	$C_6H_3(CH_3)_2(C_2H_5)$		++	
CO	++		++	$C_6H_4Cl_2$		+	
N_2	++	++	++	Xe	++		
NO	++	++	+	$C_{10}H_8$	+E		
C_2H_6	–	–	–	$C_6H_4(C_2H_5)_2$	+E		
Ar^{40}		++		anthracene	} E		
C_3H_8	–	–	–	phenanthrene			
CO_2	++	+		$C_nH_{2n+1}Cl$ (n = 12–18)	+	+	
C_4H_8	++	++	++	$R—SO_3—CH_3$	+E		
COS	++	++		trimethylanthracene or trimethylphenanthrene	E		
SO_2	++						
CS_2	++		++	alcohols	?	?	+
C_2H_6	++	++	++	aliphatic and alicyclic hydrocarbons	?	?	
Kr	++						
$C_6H_5CH_3$	++	+					
$C_6H_5C_2H_5$	+						

*The approximate abundances are denoted by one or two plus signs. The compounds which were looked for but not found are denoted by the minus sign and those detected on extraction with solvents are denoted by the letter *E*. The question mark denotes tentative compounds.

The non-equilibrium process is to a high degree non-selective with respect to the formation of particular compounds. In all the numerous experiments on this process it was found that methane is always accompanied by light alkanes, aliphatic compounds predominate over aromatic compounds, complex aromatic compounds, for example coronene, could not be detected at all, and the amount of branched alkanes obtained was considerably greater than that of the straight-chain isomers. Thus this process cannot explain the data obtained for the meteorites: neither the high methane : ethane ratio nor the absence of propane, butane, and pentane, nor the predominance or aromatic compounds, nor the high straight-chain alkane : branched-chain alkane ratio.

In recent years the equilibrium process did not attract attention, since thermodynamic calculations for the gas having the cosmic composition, i.e. with a very high hydrogen content, showed that in this way it is possible to obtain only traces of complex organic compounds. The first step in the demonstration of the possibilities of this process were taken by Suess[92], who pointed out that, in a gas depleted in hydrogen by a factor of 100 compared with the

† Studier et al.[91] quote the values of m/e for several dozen peaks in the mass spectra which were not identified.

cosmic abundance, complex organic compounds can form by equilibrium reactions. Subsequently this was fully confirmed by computer calculations[93,94] of the equilibrium concentrations of all the main components produced in the system carbon–hydrogen–oxygen and also of a representative group of more than 100 compounds present in small amounts. The concentrations of compounds containing nitrogen, sulphur, and chlorine in addition to carbon, hydrogen, and oxygen were also calculated. A wide range of temperatures and pressures was considered: from 300° to 1000°K and from 10^{-6} to 300 atm. The results for the carbon–hydrogen–oxygen mixture are presented in the form of a ternary diagram in Fig. 1. The straight lines separate the regions in which particular compounds predominate. The straight line in the centre of the diagram indicates the position of the "asphalt threshold", above which the concentration of aromatic compounds increases by a factor of 10^{20}–10^{30}, until finally these compounds become the main components of the system (Fig. 2). The curved lines in the lower part of the diagram correspond to the equality of the free energies of carbon in the gaseous mixture and the free energy of graphite (dashed line for 500°K and continuous line for 700°K). Above this line, complete thermodynamic equilibrium requires the formation of graphite. However, since the activation energy required for its formation is very high, considerable amounts of resins and asphalts accumulate before this happens. The points *A*, *B*, *C*, and *D* in Fig. 1 indicate the compositions of the mixtures for which the concentrations of a number of compounds have been published[93,94] (500°K and 1 atm). With these four compositions, it was found that many compounds which are biologically important, such as ribose, glycerol, and derivatives of adenine, cytosine, glycylglycine, and serine, are present at concentrations less than 10^{-35}.

Unfortunately only one of these four mixtures, mixture *O* (Fig. 1) with the ratios C : H : O = 1 : 1 : 1.33, lies above the "asphalt threshold". Studier, Hayatsu, and Anders[91] selected the compounds for which concentrations in excess of 10^{-10} had been calculated and, having arranged them in descending order, compared them with their own results (Table 6). It was found that all nine compounds which are the most abundant in mixture *C* are present in carbonaceous chondrites. The next two compounds, ethane and ammonia, were not found despite a thorough search. The upper limit of the ethane content thus found, 10^{-2} of the methane content, is higher by a power of ten than the calculated concentration. Of the remaining five compounds, only xylene was detected. Its detection is probably due to the characteristics of the sensitivity range of the mass spectrometer. In general there is a remarkable qualitative agreement between the theoretical distribution and the results of the experimental study of the volatile compounds from meteorites.

Having established that at least the major part of organic compounds in meteorites were formed in an equilibrium process, Studier, Hayatsu, and Anders posed the question of the time and place of their formation. Since meteorites are fragments of asteroids, there are three possibilities:

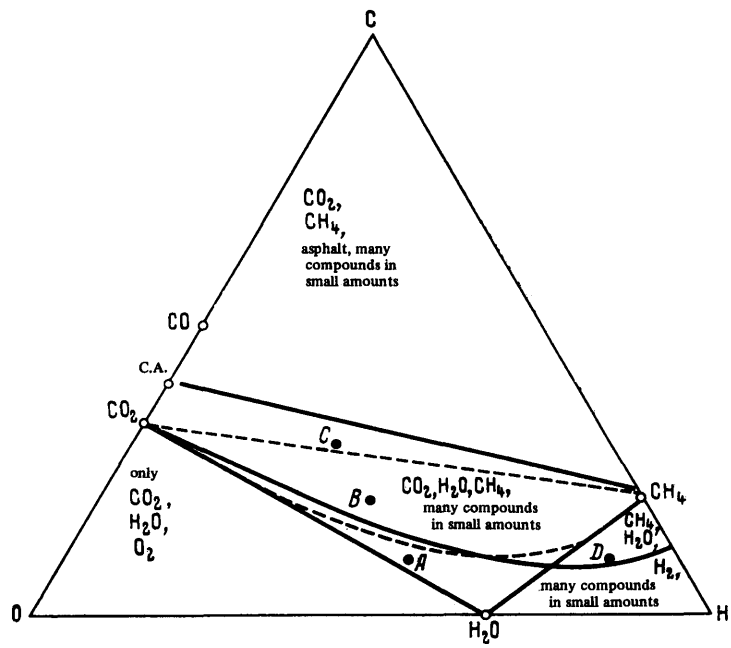

Figure 1. Ternary diagram for the system carbon–hydrogen–oxygen with the indication of the "asphalt threshold" (straight lines in the centre of the diagram) and the lines corresponding to the equality of the free energy of carbon in the gas mixture and the free energy of graphite (curved lines in the lower part of the diagram) at 500°K (dashed line) and 700°K (continuous line). The point C.A. on the O–C line indicates the ratio of the cosmic abundances of these elements.

(1) the transient atmosphere of asteroids (because of their low mass, asteroids do not have a permanent atmosphere); (2) the "internal atmosphere" (see p. 67); (3) the protoplanetary cloud. The first two possibilities must be rejected, since, in order to explain the amount of organic compounds present in meteorites, an impossibly large mass of the atmosphere is necessary—between 100 and 1000 kg of carbon dioxide and methane per cm^2. At the same time the formation of the organic compounds in the protoplanetary cloud is quite possible. The cloud having the cosmic composition coincides almost completely with the point H in Fig. 1, i.e. its composition occurs in the region where hydrogen, carbon, and oxygen are almost entirely present as H_2, CH_4, and H_2O. Along the C–O line the cosmic ratio of the abundances of these elements is represented by the point C.A. The selective loss of hydrogen alters the composition of the mixture along the C.A. line (not shown in Fig. 1) and at about 500°K the "asphalt threshold" is crossed by the mixture.

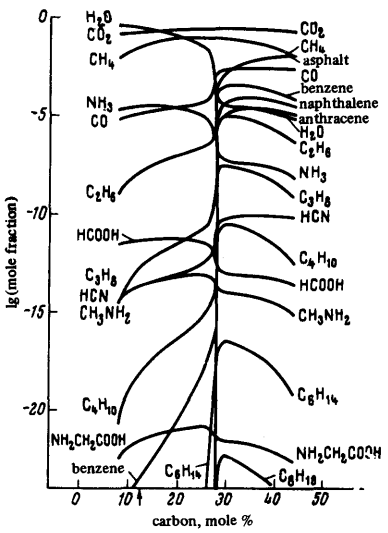

Figure 2. Variation of the concentrations of a number of organic compounds on crossing the "asphalt threshold".

The paper of Studier, Hayatsu, and Anders was very sharply critisised by Urey and Lewis and by Burlingame and Schnoes, but the criticism received an entirely convincing answer[95–97]. Urey and Lewis rejected the possibility of using the results of the calculation of equilibrium concentrations on the assumption that there is no graphite. However, in their reply Studier, Hayatsu, and Anders were already able to confirm the absence of free carbon by their experimental results obtained in the study of the attainment of equilibrium in the system carbon–hydrogen–oxygen[98]. They employed CO–H_2 mixtures, since in the temperature range 1000–200° and at moderate pressures carbon monoxide is the dominant form of carbon in the cosmic gas. In the first 15 experiments molecular hydrogen was employed but subsequently 38 experiments were carried out using molecular deuterium (D_2) to avoid the risk of contamination. The mixture compositions ranged from the atomic ratios C : H : O = 1 : 1 : 1, which corresponds to the "asphalt" region in the ternary diagram, to C : H : O = 1 : 500 : 1, which is close to the cosmic value. The principal aim of these experiments was to test the hypothesis that the formation of free carbon is inhibited kinetically, so that there arises a metastable distribution of compounds with a high proportion of aromatic components. In some series of experiments pure gas mixtures were employed and in others the catalytic effects of powders consisting of iron and stone meteorites were examined. The temperature of the gas mixture, which was usually under a pressure of 1–2 atm, was increased in steps and the compounds formed were investigated mass-spectrometrically.

Table 6.

Compound	Calc. concns. for mixture C	Presence in carbonaceous chondrites	Compound	Calc. concns. for mixture C	Presence in carbonaceous chondrites
Carbon dioxide	0.66	+	Anthracene	$2.9 \cdot 10^{-5}$	+
Nitrogen	0.50	+	Ethane	$2.3 \cdot 10^{-5}$	—
Methane	0.24	+	Ammonia	$1.1 \cdot 10^{-6}$	—
Carbon monoxide	$5.3 \cdot 10^{-3}$	+	Xylene	$9.4 \cdot 10^{-8}$	+
Benzene	$6.6 \cdot 10^{-4}$	+	Ethylene	$5.7 \cdot 10^{-9}$	
Naphthalene	$1.4 \cdot 10^{-4}$	+	Acetic acid	$1.2 \cdot 10^{-9}$	
Hydrogen	$1.3 \cdot 10^{-4}$	+	Hydrogen cyanide	$1.4 \cdot 10^{-10}$	
Water	$7.9 \cdot 10^{-5}$	+	Benzoic acid	$1.3 \cdot 10^{-10}$	

The experiments showed that the familiar Fischer–Tropsch reaction:

$$n\,CO + \left(n + \frac{1}{2}x\right) H_2 \rightarrow C_nH_x + n\,H_2O$$

took place. When this reaction is carried out under industrial conditions, the catalysts used are iron, nickel, and cobalt, i.e. precisely the elements which enter into the composition of iron meteorites. Therefore it is not surprising that the meteorite powder has a powerful catalytic effect. Without it a scarcely detectable amount of organic compounds is formed only after prolonged heating, whereas in the presence of the iron meteorite powder a wide variety of complex hydrocarbons are rapidly produced, but not even traces of free carbon were detected.

The distribution of reaction products strongly depended on time and temperature. At low temperatures the reaction did not reach equilibrium. This was shown by the fact that, for the mixture whose composition lies within the "asphalt" region, aliphatic hydrocarbons predominated over the aromatic compounds. At high temperatures and for prolonged reactions the results are closer to equilibrium, when only traces of aliphatic compounds should be detected.

On the basis of their experiments, Studier, Hayatsu, and Anders concluded that the organic compounds present in meteorites can be obtained in two stages: initially the Fischer–Tropsch reaction yields as metastable products straight-chain alkanes, methyl- and dimethyl-alkanes, alkenes, and light aromatic compounds and then equilibrium is partially attained, whereupon the amount of light alkanes falls and that of aromatic compounds and methane increases, with formation of condensed aromatic compounds (but carbon is not formed!).

This two-stage process might have occurred in the protoplanetary cloud having the cosmic composition and there is no need for its depletion in hydrogen, which initially appeared to be essential for the carbon–hydrogen–oxygen

mixture to fall within the "asphalt" region of the ternary diagram. Experiments showed that the first stage (the Fischer–Tropsch reaction) takes place satisfactorily with H:C = 500, which is close to the cosmic value of this ratio. Only during the second stage is it necessary that the composition should be in the "asphalt" region, i.e. in the region where H:C < 4. However, the organic compounds formed in the first stage correspond to H:C ≤ 2; when they condense and are thereby virtually isolated from the hydrogen-rich gas phase, they automatically fall within the "asphalt" region. The organic compounds formed condensed on the surface of dust particles, where the second stage of the process took place.

The experiments of Hayatsu et al.[99] showed that nitrogen-containing organic compounds might have formed in the same two-stage process if the latter took place in the presence of ammonia.

Modern hypotheses concerning the formation of the protoplanetary cloud by separation from the protosun in the final stage of its contraction entail a hot brief initial stage during which carbon must have existed in the form of carbon monoxide. When the cloud cooled, the condensation of metallic and silicate dust particles created catalytic centres for the Fischer–Tropsch reaction between carbon monoxide and molecular hydrogen. Because of the presence in the protoplanetary cloud of nitrogen, sulphur, and chlorine, not only hydrocarbons but a wide variety of organic compounds might have formed. These compounds condensed on the surface of the dust particles and together with them entered into the composition of the parent bodies of the meteorites formed by accretion from the dust component of the protoplanetary cloud. The second stage of the process—the partial attainment of equilibrium—probably occurred within the interior of these parent bodies—in that part of their material which was subjected to even slight heating and which gave rise to carbonaceous chondrites.

Investigators adhering to the idea of the biological origin of organic compounds present in meteorites for some reason do not discuss the question of what were the involatile carbon compounds which entered into the composition of the parent bodies of the meteorites and served, from their point of view, as the raw materials for further biological synthesis. The work of Anders and coworkers shows that the principal features of meteoritic hydrocarbons are characteristic of the abiogenic material synthesised from carbon monoxide and molecular hydrogen.

Studier, Hayatsu, and Anders note that the similarity between meteoritic and terrestrial hydrocarbons, including biogenic hydrocarbons, is frequently exaggerated and also that the importance of this similarity is overestimated. In this connection they point to the work of Friedel and Sharkey[100,101], who showed that the abundance of different isomers in crude petroleum from Saudi Arabia is expressed by the same formula as their abundance in the products of the Fischer–Tropsch reaction. This formula involves only two adjustable parameters, namely the probability of increase in chain length and the probability of chain branching. This shows that the distribution of isomers in crude petroleum is not due to biosynthesis but to catalytic processes and therefore the similarity between terrestrial and meteoritic hydrocarbons does not constitute evidence for the biological origin of the latter. On the contrary, this may be regarded as evidence for a non-biological origin of a considerable proportion of terrestrial petroleum.

Thus considerable advances have now been achieved in the study of organic compounds present in meteorites and the principal features of their abiogenic synthesis in the protoplanetary cloud have been elucidated.

5. ORGANIC COMPOUNDS ON EARTH

The presence of abiogenic organic compounds in meteorites and consequently in the parent bodies of the meteorites (asteroids) makes it virtually certain that these compounds were also present in the material from which the earth accumulated. Judging from type I carbonaceous chondrites, the total mass of the "primary" organic compounds brought to the earth might have exceeded severalfold the mass of water in the oceans[27,102].

However, only a small fraction of the "primary" organic compounds could persist in the course of the formation of the earth and its subsequent evolution. In the first place the "primary" organic material broke down to a considerable extent as a result of the temperature rise accompanying the impact of planetismals against the surface of the growing earth. However, Studier, Hayatsu, and Anders believe that, during the dispersion and cooling of the products of the "explosion" accompanying the impact, new hydrocarbons and other organic compounds might have formed rapidly (as a result of the Fischer–Tropsch reaction and other processes occurring simultaneously). Nevertheless the newly formed compounds and the persisting portion of the "primary" compounds from the protoplanetary cloud were buried in the course of the further growth of the earth underneath the growing outer layers. At the same time the interior of the earth, starting with a depth of the order of 100 km, became hot, initially as a result of the evolution of the energy associated with the accretion process itself and then as a result of the accumulation of heat due to radioactivity. At the present time the temperature of the interior is 2000–4000°C and this should probably result in an almost complete breakdown of organic compounds. The material of meteorites of most types was heated to 500–1000°C and organic compounds are present in the latter in amounts corresponding to hundredths and thousandths of a per cent. (However, it should be noted that, although this content is smaller by 2–3 powers of ten than in carbonaceous chondrites, it is nevertheless of the same order of magnitude as the content of organic compounds in terrestrial rocks, frequently regarded as petroleum bearing.)

The "primary" organic compounds and the compounds formed during the dispersion of material after the impacts of planetismals might have partially persisted only in outer relatively cold layers of the earth. Furthermore new compounds might have been synthesised in these layers from the decomposition products diffusing from the hot interior to the surface. It has been shown experimentally that clays are good catalysts for the Fischer–Tropsch reaction[103].

Thus it appears very probable that a considerable proportion of the pre-biological organic matter on earth was not formed by the Mueller–Urey reaction in the terrestrial atmosphere but by Fischer–Tropsch reactions both in the protoplanetary cloud and during further stages in the evolution of the main bulk of terrestrial material. As early as a few years ago, a number of authors pointed out that the formation of organic compounds must have begun in the protoplanetary cloud[43,47,104–108].

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The studies carried out in recent years have significantly extended and deepened our knowledge concerning the presence of organic compounds, ranging from the simplest to the most complex, in various bodies in the solar system. The studies of the organic material from meteorites,

which demonstrate the presence in the latter of very complex organic compounds, frequently encountered in terrestrial biogenic organic materials, are particularly important.

Modern astronomical data quite definitely indicate that meteorites are fragments of parent bodies on which conditions necessary for the occurrence of life did not exist and therefore the organic material of the meteorites has an abiogenic origin. Thus the presence of complex organic compounds in meteorites demonstrates the wide possibilities of abiogenic synthesis of organic compounds under natural conditions.

The data on the organic compounds in meteorites together with the advances in the laboratory synthesis of organic compounds, and in planetary cosmogony as regards the formation of the earth, provide a basis for the revision of our hypotheses concerning the complexity attained by the abiogenic synthesis of organic compounds on earth before the generation of life led to the occurrence of biological synthesis, and also concerning the role of natural abiogenic syntheses at the present time.

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Shmidt Institute of Terrestrial
Physics, USSR Academy of
Sciences, Moscow

U.D.C. 621.175

The Spontaneous Condensation of Vapour and the Formation of Condensation Aerosols

A.G.Sutugin

The development of the theory of spontaneous condensation of vapour, experimental studies of this phenomenon, and the use of the theoretical results for calculations on the formation of condensation aerosols are reviewed. The difficulty of calculating the free energy of formation of the nuclei of a new phase is examined in detail, and particular attention is paid to the problem of the contribution made by external degrees of freedom to the free energy. The problem of the existence of limiting supersaturation is discussed. Existing methods for the study of spontaneous condensation and the results obtained by these methods are examined critically. The bibliography contains 191 references.

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I. INTRODUCTION

The spontaneous (homogeneous) condensation of vapour, first examined at an early date by Gibbs, has recently been attracting increasing attention from specialists working in various fields of science and technology. Spontaneous condensation takes place in various important technological processes, in powder and vacuum metallurgy, in rocket jets, and in supersonic aerodynamic nozzles. The results obtained in the study of the condensation of vapour are important for an understanding of the mechanism of other first-order phase changes taking place in the solidification of alloys, boiling, cavitation, the crystallisation of polymers, the devitrification of glasses, and the separation of phases on a spinodal; the results are also important for the theory of the equation of state of gases. The number of papers devoted to this problem is increasing, and there is also an increase in the number of different views regarding fundamental problems of the theory, such as the determination of the free energy of nucleus formation, the accomodation of molecules on the surface of the nuclei, and the influence of the association of the condensing vapour. Reviews on this problem, published chiefly in other countries, generally do not deal objectively with some aspects. In the last two decades, new experimental methods for studying spontaneous condensation have appeared, but the results of these studies have been inadequately dealt with in the review literature. At the same time, experimental practice is requiring the development of theoretical methods of calculation which will make it possible to predict the course of the production of the particle distribution with respect to dimensions in condensation aerosols, since it is only when such methods have been developed that deliberate control of this process will be possible. The present review is devoted to a critical examination of modern theories of spontaneous condensation, experimental methods of study, the relationship between theory and experiment, and methods for calculating the microscopic model of aerosol formation.

II. THE PRESENT STUDY OF THE THEORY OF SPONTANEOUS CONDENSATION

The theory of spontaneous nucleus formation in a supersaturated vapour, developed by Volmer[1], Farkas[2], Becker and Doring[3], and in its most elegant and complete form by Zel'dovich[4,5] and Frenkel'[6,7], has long since become classical, and has been described in many reviews and monographs[8-10]. This theory is based on the model first proposed by Szilard and Farkas[2], according to which a supersaturated vapour consists of a mixture of single molecules and molecular aggregates (clusters), which, according to Frenkel', can be regarded as the nuclei of a new phase. In the present review the term "nucleus" will be used only to denote aggregates of supercritical dimensions, that is dimensions at which the aggregates are stable and the probability of their growth is greater than the probability of their volatilisation. According to the general theory of thermodynamic fluctuations, the number of aggregates decreases exponentially with increase in their free energy of formation ΔG. In an unsaturated vapour, the dependence of ΔG on the dimensions of the aggregate decreases monotonically, and in the supersaturated vapour it has a minimum corresponding to the dimensions of the critical cluster. In the classical theory we can express the probability $W_g(t)$ of finding a cluster at moment of time t at a certain point on the g axis (g is the number of molecules in the nucleus) by the equation for a Markovian process:

$$\frac{dW_g(t)}{dt} = \alpha_{g-1}W_{g-1}(t) - (\alpha_g + \beta_g)W_g(t) + \beta_{g+1}W_{g+1}(t) \qquad (1)$$

where α and β are the rate constants for the reactions $A_g + A_1 \rightarrow A_{g+1}$ and $A_{g+1} \rightarrow A_g + A_1$, and A_g and A_1 represent clusters consisting of g molecules and a single molecule. Under equilibrium conditions:

$$\beta_g = \alpha_{g-1}W^0_{g-1}/W^0_g \qquad (2)$$

where $W_g^0 = c_1 \exp(-\Delta G_g^0/kT)$, ΔG_g^0 is the equilibrium value of the free energy of formation of the aggregate, and c_1 the concentration of molecules. By substituting the values of W and β, and replacing the finite differences $\alpha_{g+1} - \alpha_g$ and $\beta_{g+1} - \beta_g$ by differentials, we transform Eqn. (1) into the form

$$\frac{\partial W(g,t)}{\partial t} = \frac{\partial}{\partial g}\left\{\alpha_g \frac{\partial W(g,t)}{\partial g} + \alpha_g \frac{W(g,t)}{kT}\frac{\partial(\Delta G_g)}{\partial g}\right\}. \quad (3)$$

This is essentially the Fokker–Planck equation for the diffusion of the aggregates along the g axis. It was first derived by Frenkel'. To determine the number of aggregates reaching supercritical dimensions in unit time, J, it is assumed that the process is a steady-state process, that is the quantity c_1 is kept constant, and the clusters are removed from the system when their dimensions exceed the critical dimensions g^*. We then have

$$\alpha_g \frac{\partial W(g)}{\partial g} + \alpha_g \frac{W(g)}{kT}\frac{\partial(\Delta G_g)}{\partial g} = -J. \quad (4)$$

Various authors have solved this equation and obtained a result which can be written in the general form:

$$J = 4\pi r^{*2}(p/\sqrt{2\pi mkT})\, c_1 Z \exp(-\Delta G^*/kT) \quad (5)$$

where $p/\sqrt{2\pi mkT}$ is the number of collisions undergone by the molecules of the vapour with unit area of the cluster surface, p the pressure and m the mass of a molecule of the vapour, and Z the non-equilibrium Zel'dovich factor—$Z = (\Delta G^*/3\pi kTg^{*2})^{1/2}$.

This factor is of the order of 10^{-1}–10^{-2} and characterises the deviation of the concentration of the clusters from the equilibrium value. Various expressions for J are given in the Table.

The equations given in the Table show that J depends to a marked extent on the magnitude of the supersaturation S. We can therefore speak of the "critical supersaturation", that is the supersaturation at which the rate of nucleus formation becomes appreciable. The critical supersaturation is usually taken to be that corresponding to a rate of formation of nuclei equal to 1 cm^{-3} s^{-1}. For water vapour saturated at room temperature, a change in supersaturation of 15% close to the critical value produces a change in J by a factor of $\sim 10^8$, and this makes it possible to find S_{cr} from comparatively rough determinations of the concentration of the aerosol produced in the experiment. Volmer and Flood[22] obtained for the magnitude of the critical supersaturation the expression

$$\lg S_{cr} = \sqrt{\frac{1{,}44}{\lg A}}\left(\frac{M}{\rho}\right)\left(\frac{\sigma}{T}\right)^3 \quad (6)$$

where A is the pre-exponential factor in Eqn. (5) for the rate of nucleus formation.

A key feature of the theory is the determination of the free energy of formation of the cluster. In the classical theory it is assumed that ΔG can be represented as the sum of two terms—a bulk term and a surface term:

$$\Delta G = Ag + Bg^{2/3} \quad (7)$$

where $A = kT \ln S$, $S = p/p_0$, p_0 is the equilibrium pressure of the vapour at the given temperature,

$$Bg^{2/3} = 4\pi r^2 \sigma, \quad (8)$$

and σ is the surface tension, and it is assumed that the cluster has macroscopic values for the surface tension and the density ρ. This last assumption has been criticised many times. Attempts to calculate ΔG without apriori assumptions regarding the values of σ and ρ for the material of the nucleus can be divided into two main groups. In the first group, the authors have tried to express σ and ρ as functions of the dimensions of the nuclei, and in the second, various attempts have been made to calculate ΔG without the apriori assumption that this quantity can be divided into bulk and surface contributions.

Equations for the rate of nucleus formation*.

$J = a_c N^{4/3}(p/R)^2(2M\sigma/\pi)^{1/2}\exp[(-16\sigma^3M^2/3kp^2R^2T^2\ln^2 s)] \equiv \equiv A_\Phi \exp(-\Delta C_\Phi/kT) \equiv J_\Phi$	1, 5, 7, 12
$J = g^{*4/3}Z_\Phi$	3
$J = a_c(2M\sigma/N\pi)^{1/2}(p_0/kT)^2\rho^{-1}g^{*-2/3}\exp[(-\Delta H_\Phi/kT)(1-3g^{*-1/3}+2g^{-1*})]$	13
$J = A\exp[(-\Delta G_\Phi/kT)(1-2\sqrt[3]{4}g^{*-1/3}+4g^{*-1})]$	14
$J = a_c Np(2\pi MkT)^{-1/2}(4\pi d^2c^2)(kTN/\pi M)^{1/2}\exp(-\Delta C_\Phi/kT)$	11
$J = K\exp(-\Delta G_\Phi/kT)\sinh(-\alpha g^{*1/3}/3kT)$, $\alpha g^{*2/3} = 4\pi r^*\sigma$, K is a factor including the rate constant of the reaction, $A_g + A_1 \rightarrow A_{g+1}$	15
$J = J_\Phi/S$	16
$J = J_\Phi \cdot Q_t Q_r/c$	17
$J = J_\Phi Q_t Q_r (c_e/q_t)^2/c$	18
$J = J_\Phi (Q_t Q_r/c)(2\pi^* g)^{-1/2} e^{-\delta}$	19
$J = J_\Phi (Q_t Q_r/c)\, e^{\delta}(2\pi g^*)^{-1/2} S^{-1}$	20
$J = J_\Phi (Q_t Q_r/c)(c/q_t)^2(q^{*4}/S)$ for monatomic molecules	21
$J = J_\Phi (Q_t Q_r/c)(c/q_t q_r)^{1.2}(q^{*4}/S)$ for vapour consisting of linear polyatomic molecules	21
$J = J_\Phi (Q_t Q_r/c)(c/q_t q_r)(q^{*4}/S)$ for nonlinear molecules	21

*Symbols: ρ is the density of the liquid, r^* the radius of the critical nucleus, c the concentration of the molecules of the vapour, c_e the equilibrium concentration of the molecules of the vapour, a_c the accommodation coefficient, M the molecular weight, R the universal gas constant, N Avogadro's number, q_t and q_r the translational and rotational partition functions for the molecules of the vapour, Q_t and Q_r the corresponding partition functions for the critical aggregates, and d the diameter of the molecules of the vapour.

From the theory of the interphase boundary formulated by Gibbs, it follows logically that the surface tension should depend on the curvature of the surface of separation between the phases[23]. Kennan[24] put forward arguments justifying the monotonic decrease in σ with increase in the positive curvature of the surface. A quantitative expression for the relationship $\sigma = f(r)$, where r is the radius of the liquid drop, was first obtained by Tolman[25], who combined the basic equation of Gibbs' theory with the Gibbs–Kelvin equation relating the equilibrium pressure of the vapour above the drop and the curvature of the surface. By neglecting terms containing $1/r$ raised to powers > 1, Tolman obtained the following expression

$$\sigma/\sigma_0 = 1/[1+2(\delta/r)] \quad (9)$$

where δ is a quantity of the order of the interatomic distance, and σ_0 the tension of a flat surface.

Kirkwood and Buff[26] pointed out the inaccuracy in Tolman's arguments, due to the identification of the pressure

in a microscopic drop p' with the pressure in a macroscopic volume of liquid, and calculated the relationship $p'/(r)$ using Kirkwood's statistical theory, according to which the pressure in a liquid is determined by the intermolecular forces, described by the Lennard-Jones equation[27]. By taking account of only the interaction of pairs of nearest neighbours, Kirkwood and Buff obtained the same result as Tolman[25]. An even more rigorous derivation of Eqn. (9) was given by Hill[28]. As shown by Buff and Kirkwood[29], however, mere allowance for the relationship $\sigma(r)$ cannot improve the theory, since it is also necessary to make allowance for the change in the density of the drop with change in dimensions, due to the fact that the thickness of the Gibbs' interfacial layer becomes commensurate with the radius of the drop. Plesner[30] calculated the surface tension and radial density distribution in nuclei with dimensions 3–25 times greater than the dimensions of the molecule. To describe the behaviour in the drop, Plesner used Tonk's equation of state[31] for solid spheres with an attractive potential inversely proportional to the sixth power of the distance. Plesner's result is surprising—the surface tension of these droplets is independent of their dimensions and amounts to $\sim \sigma_0/3$. If we remember that the factor $\exp(-\Delta G^*/kT)$ close to critical supersaturation usually has a value $\sim e^{-50}$, we can see that a change in the surface tension by a factor of 3 corresponds to an increase in the rate of nucleus formation by a factor of $\sim 10^{15}$. Plesner's discovery that σ is independent of the curvature means that within a certain range of dimensions there should be a sharp decrease in σ with decrease in r. Since the relationship $\sigma(r)$ is not observed experimentally as far as values of the curvature equal to 10^6 cm^{-1}, this range must be fairly narrow. All this appears unlikely. An interesting feature is that, according to Plesner, very fine drops, even at their centres, do not have the same densities as macroscopic amounts of the liquid.

Shcherbakov[32,33] pointed out that the excess of free energy in very fine drops relates to the entire volume of the drop, and not merely to its surface. He also found that simple substitution of the relationship $\sigma(r)$ in Kelvin's equation cannot lead to the correct result, and that it is also necessary to introduce into this equation a term containing $d\sigma/dr$. This viewpoint was put forward by both Kelvin and Gibbs, but their opinion was based entirely on intuition. In Shcherbakov's theory, surface tension is regarded as a quantity equal to the excess free energy per unit surface area of the drop. The expression obtained by Shcherbakov for the quantity σ defined in this way has the form

$$\sigma = \sigma_0\left(1 - \frac{2}{kr} + \frac{2}{k^2r^2}\right) \qquad (10)$$

where $(1/k \simeq 0.2\text{–}0.5 \times 10^{-7}$ cm). Because of the third term, which increases with decrease in r, the function $\sigma(r)$ has a minimum, and at very small values of r it increases with decrease in the dimensions. This result does not agree with the results of published work[25-30] or with the conclusion recently reached by Bellemans[34] in a generalisation of the theory of the Mayer–Born–Fuchs equation of state[35] for the case of a system containing an interface of arbitrary curvature.

A monotonically decreasing relationship $\sigma(r)$ is also predicted by the theory of surface tension developed by Cahn and Hilliard[36,37] and Hart[38], based on the idea that the free energy density is a function of the concentration and concentration gradient of the molecules. The quantity ΔG in this theory can be calculated without introducing the surface tension, according to the formula

$$\Delta G = \int_V [f_0(c) + k(\nabla c)^2]\, dV \qquad (11)$$

where ∇c is the concentration gradient of the molecules, and $f_0(c)$ is the Helmholtz free energy for one molecule. On the spinodal, that is the line on the phase diagram whose equation, according to Gibbs, has the form

$$dP\,dV + dT\,dS + \Sigma\, dN\, d\mu = 0 \qquad (12)$$

ΔG becomes zero. As the spinodal is approached, according to this theory, the surface of the clusters becomes diffuse, and their radius tends to infinity. At low supersaturations, the Cahn–Hilliard–Hart theory predicts[38] a rate of nucleus formation close to that obtained from the classical theory. In recent years this theory has been further developed[39-42], and Hart[40] has reached an extremely important conclusion. In the Gibbs' theory of surface tension, the quantity σ is invariant with respect to the position of the interphase boundary in the intermediate range between the phases. For a curved surface, this invariance is not observed, and the calculated value of σ depends on the choice of position for the boundary between the phases. In this instance σ is found from the condition $d\sigma/dR = 0$, where R is the radial coordinate. Hart established that under certain conditions the function $\sigma(R)$ may not have a minimum, that is the free energy of the nucleus cannot always be separated into bulk and surface terms.

In the Cahn–Hilliard–Hart theory it is assumed that the changes in the concentration of the molecules are small at distances close to the value for the radius of action of the intermolecular forces. This assumption has been criticised by Hirth and Pound[43].

Reed[44] calculated the chemical potential of a molecular aggregate consisting of up to eight molecules by finding the sums with respect to states of the aggregates, regarding them as polyatomic molecules. He assumed that the interaction between nearest neighbours in the aggregate is described by the Lennard-Jones equation. Reed's theory is applicable to larger aggregates only with great difficulty, because of the increase in the magnitude of the calculations. In Reed's theory it is possible only to estimate the influence of the presence of isomeric configurations of the aggregates, consisting of the same number of molecules, on their equilibrium concentration. Kilpatrick and Katsura[45] developed a method for calculating the virial coefficients of vapours containing aggregates consisting of several (up to ten) molecules. This makes it possible to calculate the equilibrium values of the free energy of formation of these aggregates. Benson and Shuttleworth[46] calculated the free energy of a cluster containing 13 molecules, assuming that the molecules in the nucleus are close-packed, and making allowance only for the interaction of pairs of nearest neighbours.

In view of the successful development of work on the many-body problem[47], we can expect the development of a nucleus model in which the treatment is not restricted to the interaction of nearest neighbours.

In recent years, the problem of the contribution of the external degrees of freedom of the cluster to its free energy has been widely discussed. This problem was first examined by Frenkel'[48]. Having pointed out that the result obtained by the theory of nucleation without allowance for the contribution made by the rotational and translational movement of the cluster to the value of ΔG has no physical significance, Frenkel' assumed that in order to

take account of this contribution it is sufficient to exclude six internal degrees of freedom. For this purpose he replaced g by $g - 2$ in the expression for ΔG (7). The exclusion of six internal degrees of freedom in order to take account of the external degrees of freedom is quite logical, but for this purpose it would be sufficient to replace g by $g - 2$ only in the first term, that is the bulk term, in expression (7). Frenkel' did not introduce any arguments to explain why he carried out this substitution in both terms; this substitution produces almost no change in the value of ΔG, whereas replacement in only the bulk term would lead to an increase in the rate of nucleation by a factor of $\sim 10^{20}$.

Rodebush[17], in an examination of the problem of the absolute entropy of formation of clusters, also concluded that it is necessary to make allowance for the external degrees of freedom, but he subsequently concluded[40] that this contribution is taken into account automatically in the classical theory. Adams and Band[50] made allowance for the contribution of the translational degrees of freedom, neglecting rotational degrees of freedom. As pointed out by Kuhrt[18], with the introduction of a factor taking account of the external degrees of freedom into the statistical sum, it is necessary at the same time to exclude six vibrational degrees of freedom. The introduction of Kuhrt's correction for the example of the condensation of water vapour at supersaturations close to the critical supersaturation corresponds to an increase in the rate of nucleation by a factor of $\sim 10^8$.

Courtney[16] made allowance for the partial pressure of the clusters in the calculation of ΔG, and this led to an increase in the expression for J given by Frenkel'by a factor $1/S$, which may reach very large values at the concentration of the vapours of non-volatile substances. In his next paper[21], Courtney combined this result with Kuhrt's conclusions[18]. The expression which he obtained is given in the Table.

The problem of the absolute entropy of formation of nuclei was examined in detail by Lothe and Pound[19], Sundquist and Oriani[20], Hirth[51], Feder and coworkers[52], and Russell and coworkers[53]. The last of the works cited gives a logical summary of earlier work and formulates the following scheme, which makes it possible to find the free energy of formation of a cluster: n nuclei, containing g molecules, are formed from ng molecules of the vapour by five processes: 1) the vapour is compressed until saturated; 2) the vapour is condensed to liquid at constant temperature and pressure; 3) the liquid is supercooled to 0°K; 4) the liquid is divided reversibly into n portions; and 5) the clusters are heated to a temperature T.

By writing expressions for the changes in free energy corresponding to these processes, the authors cited[19,20,51-53] obtained an expression for the free energy of formation of a cluster. The equations which they obtained on this basis for the rate of nucleation are also given in the Table. These expressions give values for J which are greater by factors of 10^{17}–10^{18} than those obtained by Frenkel's solution. It should be noted, however, that despite the strictly logical nature of the arguments cited above, the numerical estimates of the influence of the contribution of the external degrees of freedom to the rate of nucleus formation, made in the works cited[19,20,51-53], are of doubtful accuracy. In the calculation of the term corresponding to the fifth stage in the above scheme, the authors cited mechanically applied the formulae for the translational and rotational components of the heat capacity of polyatomic molecules. A cluster, however, is a much looser formation than a polyatomic molecule, since the energy of the van der Waals' forces holding the molecules in the nucleus is much less than the energy of valency bonds. Thus, as pointed out by Vukolovich[54], the rotation of the cluster as a whole can be neglected. The theory developed by Vukolovich for the heat capacity of water vapour containing molecular associates, which ignores the external degrees of freedom of the associates, shows such good agreement with the experimental data that it has been possible on this basis to construct an accurate water vapour phase diagram, which has been widely used for several decades in technical calculations. Hirth and Pound's argument[10] that the rate of nucleus formation may be much less than the calculated value, since the probability of attachment of molecules may decrease considerably with increase in the curvature of the surface, reaching values as small as 10^{-17}, does not appear convincing. It is true, however, that Okuyama and Zung[55] predicted theoretically a decrease in the accommodation coefficient a_c for a drop radius $\leq 10^{-5}$ cm, but in their calculations they ignored the relationship $\sigma(r)$, which may weaken this effect considerably. It follows from the experimental data of Wakeshima and Takata[56] that a_c increases slightly with decrease in r.

Recently, the previously published conclusions[18,19,50-52] were convincingly criticised by Reiss and Katz[57], who showed that there is no justification for the assumption made by Lothe and Pound and subsequent workers that the expression (7) given for the value of the free energy of formation of a nucleus corresponds to an aggregate with a stationary centre of mass. After examining the classical theory in detail, Reiss and Katz concluded that it ignores only the contribution of the translational motion of the centre of mass. It is evident that this feature can be taken into account by introducing Courtney's correction $1/S$ into the expression for J. The other inaccuracy which they detected requires the introduction of a factor V_g/gV_1, where V_g is the volume of a cluster consisting of g molecules, and V_1 the volume of a single molecule. According to the estimates made by Reiss and Katz, this factor has values from 1 to 10.

Courtney[58] pointed out that even if the Lothe–Pound correction is correct, it does not mean an increase in the rate of nucleus formation by a factor as large as 10^{17}, since in this instance the greater part of the mass of the vapour should be present in aggregates with subcritical dimensions. The marked decrease in the concentration of single molecules of vapour resulting from this feature should be accompanied by a decrease in the equilibrium concentration of critical nuclei, and hence by a decrease in J.

In a number of recent papers, the determination of the rate of nucleus formation in first-order phase changes is examined on the basis of the general relationships of the thermodynamics of irreversible processes[52,59], but the conclusions reached in these papers are so general in character that it would be premature to discuss the results obtained in this direction.

The classical theory neglects the heating of the nuclei by the liberated heat of condensation. This is quite justified when the condensing vapour is a small impurity in a noncondensing gas, in which the collision of the molecules of the gas with the nuclei ensures dissipation of the heat of the phase change, but in practice we often have to deal with the condensation of vapour in the absence of a carrier gas, and the neglect of the heating effect becomes unjustified. Russell and Feder[52] solved the problem of nonisothermal formation of nuclei by examining the equation for the two-dimensional diffusion of clusters in the g–ϵ plane, where ϵ

is the thermal energy of the cluster. Similar work was carried out by Bakhanov and Buikov[60].

All the expressions given in the Table describe nucleus formation under steady-state conditions. In a non-steady-state process, however, J is a function of time t. The problem of nucleus formation in non-steady-state conditions, arising in the instantaneous production of supersaturation, has been examined by a number of authors, including Zel'dovich[5], Collins[61], Wakeshima[62,63], Kantrowitz[64], and Frisch[65], who solved a time-dependent equation of form (3), with the assumption that at the initial moment of time the vapour is completely monomolecular and that the diffusion coefficient along the g axis:

$$D = (36\pi)^{1/3} v g^{1/3} p / \sqrt{2\pi m k T} \qquad (13)$$

is independent of g. Here, v is the volume occupied by one molecule in the liquid. The result obtained by these authors can be written in the form

$$J = J_0 \exp(-k^2/zt) \qquad (14)$$

where z is the rate of growth of the particles in molecules per second, and k a constant whose order of magnitude is equal to that of the number of molecules in the nucleus. The specific values obtained by different authors[5,61-64] for the time interval $\tau_{0.9}$ after which J reaches values equal to 0.9 times its steady-state value, differ considerably; the values lie in the range 10^{-5}–10^{-6} s, and $\tau_{0.9}$ increases with decrease in the probability of attachment. Wakeshima[62] and Frisch[65] tried to make allowance for the influence of associates in the vapour on the rate of attainment of the steady-state. Wakeshima found that in this instance the rate of attainment of the steady state is increased, but Frisch reached the opposite conclusion. It should be noted that there is an error, pointed out by Courtney[66], in Frisch's mathematical calculations.

To estimate the time required for steady-state conditions to be established, it is necessary to alter the relationship $J(t)$. It is possible to determine the time interval after which the concentration of critical nuclei reaches, let us say, 50% of its steady-state value. Andres and Boudart[67] solved Eqn. (3) by the method of statistical moments. The values which they obtained for $\tau_{0.5}$ are smaller by an order of magnitude than the values of $\tau_{0.9}$ obtained by other workers[3,62-65]. A simple approximate expression for $\tau_{0.9}$ was obtained by Farley[68]:

$$\tau_{0.9} = 25 g^{*2} \sqrt{2\pi m k T} / 4\pi r^{*2} \rho$$

A third method for studying the problem of the attainment of the steady state involves numerical solution of a system of equations of type (1) for all values of g from 1 to a certain value of $g > g^*$. The first attempts of this kind were made by Christiansen[69] and Turnbull[70], who solved systems of 4 and 25 equations respectively. Courtney[71] used a computer to solve a system of equations describing the changes with time in the concentrations of clusters containing from 20 to 120 molecules. The calculations were carried out for the condensation of water vapour at −10°, −40°, and −60°C and supersaturations of 5.0 and 6.0. Courtney assumed that for nuclei with $g < 20$ the equilibrium concentration is reached instantaneously. Under these conditions, $\tau_{0.95}$ amounted to 1.5–27 μs. This is smaller by a factor of about 2–3 than that obtained from the published relationships[62-65] and is fairly close to the values which can be obtained using Farley's formula[68]. For values of $S = 5$, Courtney obtained values of $\tau_{0.95}$ which were smaller by a factor of ~ 10 than those obtained for $S = 6$. The calculations were carried out with the assumption that $a_c = 1$.

Chakraverty[72] recently solved Eqn. (3) without making any assumptions regarding the quantities α_g and β_g, which were regarded as unknown functions of g. His results show qualitative agreement with Courtney's conclusions[71] and order of magnitude agreement is also observed in the values of τ.

As pointed out by Sutugin and Fuchs[73], steady-state conditions are not attained in practice at very high supersaturations, since the supersaturation changes considerably throughout the entire process of nucleation, whose duration may not exceed 10^{-5} s. Under these conditions, calculation of nucleus formation is possible only by solving a system of equations of type (1). The problem is then simplified, since under conditions of high supersaturation the dimensions of the critical nucleus are very small and the number of equations in the system is also small. Moreover, the total duration of the process becomes commensurate with the time interval within which the nucleus collides with an average of one molecule of the vapour. This makes possible a simple calculation of the quantity of vapour involved in molecular collisions with nuclei with all dimensions represented, and also with the growing supercritical particles, and this makes it possible to avoid the assumption, which is usually made in the classical theory, that the supercritical particles are removed from the system and replaced by an equal mass of vapour.

An attempt to make allowance for the influence of the heat of condensation during the attainment of the steady state was made by Probstein[74], who expressed the probability of volatilisation of a molecule from the growing nucleus as follows:

$$\beta_g' = \beta_g \left[1 + \theta \frac{U_\infty}{RT^2} \right] \qquad (15)$$

where β_g is the probability of volatilisation under isothermal conditions, U_∞ the heat of condensation, $\theta = J_g U_\infty c m / f_g F \alpha_g a_c l$, f_g the distribution function for the concentrations of the clusters, and l the heat capacity. Probstein introduced a new time $t' = t/[1 + U_\infty^2 c_1 m / l a_c R T^2]$ and solved Eqn. (3). The method of solution which he used is analogous to the method of Kantrowitz, but since allowance was made for the heat of condensation it was found that the attainment of the steady state requires a time interval which is several times larger. As pointed out by Feder and Russell[52], a fundamental study of the problem of non-steady-state nucleus formation under nonisothermal conditions requires the solution of a three-dimensional diffusion equation in g–ϵ–t space, and this presents insurmountable difficulties. The approximate estimates which they made showed that the liberation of the heat of condensation during the formation of nuclei in water vapour under the conditions which usually exist in experiments with a Wilson chamber may lead to an increase in $\tau_{0.9}$ by a factor of 2–3 compared with isothermal conditions.

Luke[75] solved the problem of the rate of cooling of hot atoms of a metal suddenly placed in a cold inert gas. When the concentration of metal vapour is low, the excess of thermal energy of the atom is reduced by a factor of 2 in a time interval of ~ 10^{-7} s. From this it may be concluded that if the mass of condensing vapour amounts to only a small fraction of the total mass of the vapour–gas mixture, the liberation of the latent heat of the phase change may not have a marked influence on the value of J.

On going to the problem of limiting supersaturation, it is necessary first of all to note that there are at least two interpretations of this concept. The first interpretation is related to the fact that the dimensions of the cluster

cannot be less than the distance between the centres of the molecules in the liquid (or the solid). This was first pointed out by Frenkel'[7], whose viewpoint was supported by other workers[76-78] who tried to calculate the maximal supersaturation using the Gibbs–Kelvin equation, which obviously cannot be used for this purpose. Bykov and Teverovskii[76] assumed that the weak dependence of the rate of nucleation in water vapour on its supersaturation, observed by a number of workers, can be attributed to the attainment of limiting supersaturation. In Bykov and Teverovskii's own experiments, however, only the magnitude of the critical nucleus calculated according to the Gibbs–Kelvin equation remained constant, and the rate of formation of the nuclei changed considerably with change in the supersaturation.

The second concept of limiting supersaturation is based on the idea that under certain conditions the work of formation of the nucleus should become zero. The theory of second-order capillary effects, developed by Shcherbakov[79] and the Cahn–Hilliard–Hart theory[35-37], in particular, lead to this conclusion. From this concept it follows that the nucleus corresponding to limiting supersaturation may contain tens or hundreds of molecules. The formula put forward by Shcherbakov and coworkers[32,79] for calculating the limiting supersaturation contains the macroscopic density of the liquid. It follows from published work[35-36], however, that as the spinodal is approached the density of the nuclei decreases, approaching the density of the vapour.

A number of authors[80-82] consider that ΔG^* does not become equal to zero even on the spinodal. This view is contrary to Gibbs' classical theory of surface tension. Gibbs[12] in fact showed that the work of formation of a nucleus amounts to $\frac{1}{3}\sigma F$, where F is the surface area of the nucleus. Rusanov[83] pointed out that if σ becomes zero, ΔG should also become zero. Thus this concept should be correct at least for the condensation of vapour close to the critical point.

The conclusion that the minimal nucleus should contain much more than two molecules, that is that there is no vapour pressure with which very small aggregates can be in equilibrium, follows from the work of Shcherbakov[32,33], Bakhanov and Buikov[84], and Cahn, Hilliard, and Hart[35-37]. This conclusion is not completely general, however, since calculations[16,73] have shown that in the supersaturated rarefied vapours of substances with low volatility the minimum of the $\Delta G(g)$ relationship may correspond to dimers or even monomeric molecules. For the condensation of the vapours of these substances with low volatility, the concept of limiting supersaturation can be derived from the following considerations. Let us assume that we have a mixture of the vapour and a noncondensing gas. Let us cool this mixture along the isochore to a temperature at which the critical nucleus contains two molecules. The concentration of the dimer (with the condition that constant supersaturation is maintained) will be determined by the ratio of the rates of formation and breakdown of the dimeric molecules. With decrease in temperature the rate of the first process will decrease comparatively slowly, since the number of collisions between the molecules is proportional to $T^{1/2}$, whereas the second process stops almost completely at a certain temperature (this follows from calculations for rarefied silver vapour[73]). Thus the rate of formation of the critical nuclei—dimers—will first increase due to the decrease in the rate of breakdown, and then decrease as a result of the decreased number of collisions between individual molecules. Limiting supersaturation, at which the rate of nucleus formation is determined exclusively by the frequency of the collisions between individual molecules, can be obtained only in the condensation of a vapour with a sufficiently low partial pressure, otherwise exhaustion of the vapour phase takes place during the cooling of the vapour–gas mixture.

In Kachurin's opinion[85], at high supersaturations the rate of nucleus formation should be appreciably greater than that obtained in the classical theory, since in this instance, in addition to the gradual increase in heterophase fluctuations, we may have conversion of homophase fluctuations (that is fluctuations not exhibiting the structure of the new phase) into heterophase fluctuations. On the other hand, it follows from the Cahn–Hilliard–Hart theory[36-38] that as the spinodal is approached the difference between homophase and heterophase fluctuations should disappear.

As already noted, the classical theory considers only the condensation of a one-component monomolecular vapour. The vapours of most substances, however, consist of mixtures of associates. A generalised equation taking account of the possibility of collision with one another for associates and subcritical nuclei of different dimensions can be written in the form

$$\frac{dW_g}{dt} = -\sum_{j=0}^{N+1} K_{jg}W_g + \sum_{j=0}^{N} K_{gj}W_j, \quad g, j = 1, 2 \ldots N$$

where Kjg is the probability of conversion of nucleus j into g, and K_{gj} the probability of the reverse change. The analytical solution of this equation presents considerable difficulty. Frisch and Willis[86] carried out the analytical solution of a simplified equation describing nucleus formation in a vapour consisting of a mixture of the dimer and monomer. Courtney[21] used numerical methods for the same purpose. According to his results, nucleus formation should take place several times more rapidly in the presence of dimers. As correctly pointed out by Katz and Salsburg[87], however, the authors cited[21,86] neglected the decrease in supersaturation due to the fact that part of the mass of the vapour is included in the dimer. In fact, the equilibrium concentration of critical nuclei is proportional to the concentration of monomolecular vapour [(Eqn. (2)], so that association should decrease the rate of nucleus formation. An analogous conclusion was reached by Sutugin and Fuchs[73], who calculated the condensation of silver vapour for the conditions where an appreciable proportion of the condensing substance is included in subcritical associates.

Nucleus formation in a two-component condensing vapour has been examined theoretically by Neumann and Doring[88] and also by Reiss[89].

In addition to the above theory, based on the Szilard–Farkas model, attempts have been made to develop other theories of phase transformations. Expressions for the equilibrium concentrations of nuclei are obtained in the Mayer–Born–Fuchs equation of state theory[38]. The general form of these expressions is similar to that of Frenkel''s equation for the equilibrium concentration of a nucleus with given dimensions, but the determination of the equilibrium concentrations in the Mayer–Born–Fuchs theory requires extremely tedious calculation of the so-called group integrals, which take account of the contribution of the interaction between pairs of molecules making up the cluster to the statistical sum for the cluster. The problem is complicated considerably by the need to calculate the group integrals for all possible isomeric configurations. Recently, however, considerable progress has been made in this direction. Kilpatrick and Katsura[45] and Barker and Leonard[90] developed a relatively simple method for calculating the group integrals for nuclei

containing up to ten molecules. These authors were able to calculate even the fifth virial coefficient of a gas containing associates. Since during condensation the concentrations of small ($g < 10$) nuclei are almost the same as the equilibrium concentrations, the latest results of the theory of the equation of state may be useful for calculations of nucleus formation at high supersaturations.

In the opinion of Christiansen[91] and La Mer[92], the nucleus of liquid phase in a vapour should contain not more than 4–5 molecules, which is considerably less than the number assumed in the classical theory. They also assumed that for each substance the dimensions of the nucleus should depend very little on temperature, the concentration of the molecules of the vapour, and the supersaturation. Courtney[93] described this model as the "constant-number theory" and pointed out that it should be suitable for the description of nucleus formation in substances with a high intermolecular interaction potential. Sutugin and Fuchs[73] calculated nucleus formation in silver vapour condensing as a result of the cooling in a submerged stream at concentrations of 10^{16}, 10^{15}, and 10^{14} molecules cm^{-3}, and found that the dimensions of the nucleus should correspond to 5–6 molecules for the first two concentrations. For the third concentration, the rate of nucleation became appreciable when the nucleus contained six atoms, after which the cross-section of the nucleus decreased with increase in supersaturation, and for the greater part of the total duration of the process the nucleus consisted of only two atoms. For all three concentrations, the supersaturation increased by several orders of magnitude during nucleus formation. From this it follows that at high supersaturation the dimensions of the nucleus in fact change little.

Independent attempts to develop a theory of nucleus formation which does not make use of the Szilard–Farkas model have been made by Reiss[94] and Hill[95], but the models which they have proposed have been insufficiently developed, and it would be premature to discuss their importance.

Results useful for an understanding of the initial stage of the formation of associates were obtained by Storgyn and Hirshfelder[96], who examined the problem of the lifetime of a combination of two molecules, formed by the collision of two single molecules, or, in other words, the problem of the duration of collisions in pairs. These authors calculated the duration of the collisions of pairs in inert gases, with the assumption that the interaction between the molecules is described by the Lennard-Jones equation. The method which they developed makes it possible to calculate both the kinetics of formation of the dimers and their equilibrium concentration, but only by using computers.

Vukolovich's equation of state theory[54] was used by Nikandrov[97,98] to calculate the concentration of aggregates in water vapour for $S = 1$.

All that has been said in this section refers to the formation of the nuclei of a liquid phase in vapours, but since experimental data indicate that the particles of condensation aerosols are amorphous, particularly when the condensation takes place at high supersaturations[99–103], it may be assumed that in most instances the condensation of a vapour in bulk leads to the formation of nuclei of a liquid phase, which can crystallise only subsequently. According to data obtained by different authors, the condensation of water vapour below −40°C or below −65°C leads to the formation of ice nuclei, but this has been disputed by Dufour and Defay[104], who considered that ice is formed only by the freezing of water droplets produced from the vapour.

Unlike the nuclei of the liquid phase, crystalline nuclei are characterised by anisotropy of the surface energy. Because of the small dimensions of the nuclei, a marked contribution to the surface energy is made by the apices, edges, steps, and fractures on the surface of the faces. The growth of droplet nuclei includes only one process—the adsorption of molecules from the vapour phase—whereas the formation of a crystallite should include four molecular processes: the adsorption of molecules of the vapour on the surface, the nucleation of two-dimensional discs on the surface of the faces, surface diffusion, and the attachment of molecules to elementary steps, the free energy of formation of the crystallite being a monotonic function of the number of molecules of which it is made up. Stranski and Kaischev[105,106] and Carrera and Burton[107] examined the process of crystal formation, taking account of only the formation of two-dimensional discs on the faces, and assuming that in nucleation the concentrations of the clusters are equal to the equilibrium concentrations. An expression for the rate of formation of crystalline nuclei, including a non-equilibrium factor, was obtained by Becker and Doring[3,108], who calculated the bond energy of the nucleus using a model involving the interaction between pairs of nearest neighbours. Taylor[109] solved the problem of the bond energy for the crystalline nuclei of alkali metal halides, containing up to 13 molecules, by means of the quantum theory of first-order perturbations. When calculating the free energy of crystalline nuclei, as for the nuclei of a liquid phase, it is necessary to take account of the contribution made by the external degrees of freedom.

III. METHODS OF CALCULATING THE FORMATION OF CONDENSATION AEROSOLS

In the formation of a condensation aerosol, the formation and condensation growth of nuclei take place simultaneously. The consumption of vapour for the growth of the particles leads to a decrease in the supersaturation, and nucleation stops. Thus the calculation of the number and dimensions of the particles formed should make allowance for both these processes, and also for coagulation at high concentrations of the particles formed.

Calculation methods of this kind are required for comparing theory with experiment, and also for predicting the parameters of aerosols formed in various technological processes.

Existing methods of calculation can be divided into analytical and computational. The analytical method for calculating the formation of an aerosol during the adiabatic expansion of a gas containing the vapour of a condensable substance was first developed by Tunitskii[110], who carried out the simultaneous solution of the equations for conservation of mass of the condensing substance and for rate of formation of nuclei, assuming the temperature to be constant. He obtained two expressions for the number of drops formed. In the derivation of one of these expressions it was assumed that the rate of growth of the drops is determined by a gas-kinetic mechanism, and in the second instance a diffusion mechanism was assumed. Tunitskii also estimated the error introduced by neglecting the heat of condensation.

Oswatitsch[111,112] developed an analytical method for calculating the change in the number of drops and the mass of condensate during the condensation of vapour in a Laval nozzle. For this purpose he carried out the simultaneous solution of four differential equations: the continuity equation and the equations for the preservation of momentum,

preservation of energy, and condensation. The problem of aerosol formation during the adiabatic cooling of a vapour–gas mixture was also solved by Corner[113], and later by Bakhanov and Buikov[60], who took account of heat exchange with the external medium and the change in temperature resulting from the heat of condensation. Any of the steady-state solutions for the rate of nucleus formation can be used in any of the above methods of calculation.

Raizer[114] solved the problem of condensation in a cloud of vapour undergoing adiabatic expansion into a vacuum, but he neglected the liberation of the heat of condensation, and this is inadmissible in the examination of condensation in the absence of a noncondensing gas capable of dissipating the energy of the phase change.

Disadvantages common to all analytical methods of calculation include the need for simplifying assumptions in the derivation, and also the fact that these methods can predict only the number of particles formed and their mean dimensions, and not the parameters of the size distribution. Analytical methods of calculation cannot include an examination of coagulation. In the calculation of the growth of the particles it is necessary to assume that throughout the entire process, growth takes place by a single mechanism, whereas the mechanism changes with increase in the dimensions of the particles. An analytical solution is also impossible if the temperature and concentration are functions of more than one variable[115–117]. Because of these features, methods for the successive calculation of the condensation, in which the duration of the process is broken down into tens or hundreds of intervals or stages, have been widely used. It is assumed that in each range of temperature, the concentration and other significant parameters remain constant, and that they undergo sudden changes on going to the next interval. The number of nuclei formed in each interval, and the growth of the particles previously formed, are calculated.

Amelin[118] described a program for calculating the condensation when a turbulent vapour–gas stream is cooled in a heat exchanger, Griffin and Sherman[119], Stever[120], and Hill, Wittig, and Demetri[121] described in detail stepwise methods for calculating the condensation in Laval nozzles, and Lund and Rivers[122] described methods for calculating the condensation in a Wilson chamber.

In the works cited, the calculations were carried out for situations where the supersaturation depends only on time or only on the coordinate. Higuchi and O'Konski[123] put forward a method for determining the number of nuclei formed in the zone in which a hot inner stream mixed with a cold surrounding gas. They expressed the number of particles formed in unit time by means of the integral $\int_0^\infty J(n)\frac{dV(n)}{dn}dn$, where $V(n)$ is the volume of the mixing zone bounded by a surface with constant value n, that is the ratio, averaged with respect to time, of the weight concentrations of the cold and hot gases. Higuchi and O'Konski neglected the quantity of vapour used up in the growth of the particles, and assumed that the supersaturation falls below the critical value entirely as a result of the dilution of the condensing mixture by fresh portions of cold gas. This is quite justifiable, if the supersaturation exceeds the critical value only in a very small part of the mixing zone of the stream S. If however high supersaturations are reached in the zone in which the hot vapour–gas stream mixes with cold air, the quantity of vapour used up cannot be neglected. Sutugin and Fuchs[73] developed a method for the stepwise calculation of the condensation in the stream, in which the entire mixing zone is broken down into intervals whose boundaries are the n-const surfaces. A program for calculating the formation of an aerosol under conditions in which fresh portions of condensing gas are formed continuously as a result of a chemical reaction in the gaseous phase was compiled by Dunham[124].

Carstens and coworkers[125] carried out a numerical estimation of the decrease in the rate of nucleus formation due to the decrease in the concentration of vapour close to the growing particles, and found that this effect is extremely small.

Friedlander[126] put forward a calculation of the formation of condensation aerosols in a submerged stream by means of the theory of similarity and calculated the dimensionless criteria, whose function should be the dimensions of the particles of the resulting aerosol. Like all methods based on the use of the theory of similarity, Friedlander's method requires the preliminary empirical determination of the dependence of the parameters sought on each of the criteria, the number of which may vary from 4 to 8. It is therefore not surprising that this method has not yet found application.

The formation of aerosols at high supersaturations is often accompanied by coagulation, and, as pointed out by Petryanov and Tunitskii[127], it is coagulation which should determine the degree of dispersion of the aerosols formed under these conditions. As a rule, polydisperse aerosols are formed during spontaneous condensation. A number of recent papers[128–130] are devoted to numerical methods for calculating the coagulation of aerosols by integration of a system of equations of the form:

$$\frac{dn_i}{dt} = \sum_{j+k=i} K_{jk}n_jn_k - \sum_{l=1}^{\infty} K_{jl}n_jn_l$$

where n_i is the concentration of particles formed from i primary particles, and K_{jk} the collisional rate coefficients. The volume of the calculations increases with increase in the degree of coagulation, so that this method cannot be used to calculate the coagulation leading to an increase in the dimensions of the particles by a factor of more than ~ 100. Rosinski and Snow[131] proposed a simplified scheme for the calculation of coagulation. According to the ideas of these authors, the continuous distribution function of the aerosol particles with respect to dimensions is replaced by a discontinuous function, and it is assumed that the aerosol consists entirely of particles in which the numbers of molecules are given by the figures 2^i, where i is an integer. The collisions of particles of the 2^i classes leads to the formation of particles of the 2^{i+1} class. It is then arbitrarily assumed that the collisions of particles of classes 2^i and 2^{i-1} also leads to the formation of particles of class 2^{i+1}, but in an amount corresponding to $(2^i + 2^{i-1})/2^{i+1}$ times the number of particles of class 2^i taking part in the collisions. In the collisions of particles of classes 2^1 and 2^{i-j}, where $j > 1$, however, the dimensions of the former remains unchanged, but their number increases by a factor of $(2^i + 2^{i-j})/2^i$. This scheme was used by Stockham[132] for calculations on silver vapour, and he assumed that the collision of two atoms leads irreversibly to the formation of a twin, etc. As shown by Sutugin and Fuchs[73], this is justifiable only at sufficiently low concentrations of vapour and a high rate of cooling of the vapour–gas mixture, but since the size distribution of the aerosol finally obtained is still determined by the coagulation, Stockham's results are of undoubted value. He found that Rosinski and Snow's scheme correctly predicts the degree of dispersion of the resulting aerosols if values approximately twice those obtained in the formula for the number of collisions between gas molecules are used for the coagulation constant in the

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calculations. This last feature confirms Fuchs and Sutugin's theoretical and experimental conclusions[133] that the forces of intermolecular interaction should increase considerably the coagulation constant of highly dispersed aerosols. In later work[73], the value 2.21 was obtained for the factor corresponding to the increase in the rate of coagulation of silver particles as a result of molecular forces.

Strictly speaking, the forces of intermolecular interaction should also influence the condensation growth of highly dispersed aerosols, but the introduction of a correction analogous to Sutherland's correction can hardly be meaningful, since there are almost no data on the magnitude of the condensation coefficient and its dependence on the curvature of the surface on which the condensation is taking place.

IV. EXPERIMENTAL STUDIES OF THE FORMATION OF CONDENSATION AEROSOLS

The aim of the experimental study of this phenomenon may be the determination of the critical supersaturation for a given substance and the temperature dependence of the critical supersaturation, or the determination of the dependence of the rate of nucleation on supersaturation and the influence of various factors on this rate. The development of the size distribution of particles during the formation of a condensation aerosol is of considerable interest.

The chief difference between existing methods for studying spontaneous condensation lies in the methods for the production of the supersaturation in the condensing vapour; this may be brought about by adiabatic cooling of the vapour or vapour–gas mixture (Wilson cloud chamber and Laval nozzle), by heat exchange through the walls of the apparatus, and by mixing gas streams at different temperatures.

The oldest instrument used to study spontaneous condensation is the Wilson cloud chamber[134]. Adiabatic expansion in a Wilson chamber can be brought about by means of a piston, a diaphragm, or a bellows, or by suddenly connecting the working volume to a vacuum reservoir. A number of workers have studied the problem of the adiabatic nature of the expansion taking place in the chamber. Flood[135] concluded that the expansion is adiabatic so long as the volume of the chamber is not less than 1 litre, and the degree of expansion not less than 1.4, but Stachorska[136], using an inertia-free temperature recorder, proved that the expansion is non-adiabatic in a chamber with a volume of 1 litre even for expansions of 1.2, and concluded that it is necessary to use a chamber with a volume of 30 litre, in which Thomson's equation for the adiabatic decrease in temperature is obeyed rigorously. The use of a large chamber is also desirable in order to decrease the loss of vapour and nuclei as a result of diffusional deposition on the walls.

These features restrict the application of the Wilson chamber to the range of low supersaturations. Since at supersaturations which are not too much greater than the critical supersaturation the number of nuclei formed is limited, it is necessary to take careful precautions to remove foreign condensation nuclei (including ions) from the chamber. For this purpose the chamber is filled with a filtered gas; before the start of the main measurements, several successive expansions are carried out, and the foreign condensation nuclei become larger as a result of the condensation of vapour, and are deposited on the floor of the chamber. Ions are removed by applying an electrical field.

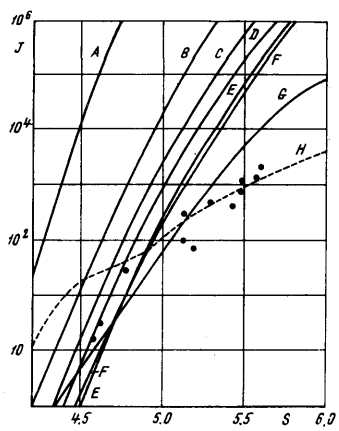
Since the end of last century, the Wilson chamber has been used many times to determine the critical supersaturation in the vapours of water, alcohols, and various other liquids, and the data obtained by its use over several decades were assumed to provide irrefutable proof of the correctness of the classical theory. Recently, however, a different viewpoint has been put forward[137–139]. Mason[137], in an examination of data on critical supersaturation obtained by Wilson and Powell[140], Volmer and Flood[141], Frey[142], Sander and Dahmkohler[143], Barnard[144], and Pound and coworkers[138], pointed out that Wilson and Powell[140] used an unsatisfactory method for detecting the start of condensation, and that the other authors cited[141–143] took inadequate measures to eliminate foreign condensation nuclei. In the much more thorough work of Barnard[144], Pound and coworkers[138], and Madonna and coworkers[139], the experimental values of the critical supersaturation coincided with the theoretical values only at temperatures $< 260°C$. Pound and coworkers[138] and Madonna and coworkers[139], like Mason[137], consider that in all work on the study of spontaneous condensation in the Wilson chamber, condensation on ions or foreign particles was in fact observed. Hollomon and Turnbull[145] found that the Volmer–Flood formula effectively predicts the critical supersaturation in the vapours of water and a number of organic liquids. Clark and Rodebush[146] found that different values are obtained for the critical supersaturation in water vapour when He or N_2 are used as inert gas. Madonna and coworkers[139] observed the same effect for the condensation of water vapour in O_2 and N_2, but Courtney[147] did not observe this effect. The scatter in the experimental values of the critical supersaturation in Courtney's work, however, was very high, even in the same carrier gas.

A number of papers have been devoted to a comparison of experimental data on the rate of nucleation with steady-state solutions of the classical theory. The rate of nucleation can be measured if the concentration of particles formed and the time interval during which they are formed are known. The first work in this direction[141,142,148,149] suffered from a large number of unsatisfactory experimental features, and the response time of the chambers in these experiments was not determined, so that it is not surprising that their results showed poor agreement with Tunitskii's calculations[110].

Stachorska[150], in a study of the condensation of C_2H_5OH vapour, obtained very good agreement with the results of his own calculations, based on Frenkel''s equation with allowance for the quantity of vapour used up in the growth of the particles. The results of Allard and Kassner[151], Kassner and Schmidt[152], and Schuster and Good[153] show good agreement with the calculations of Courtney[71] and of Lund and Rivers[154]. Although Courtney's calculations[71] were carried out using the Frenkel'–Courtney equation (see Table), whereas Lund and Rivers[154] used the Becker–Doring equation, these two equations differ only in a small numerical factor. At low supersaturations, both equations are readily justified within the limits of experimental error, but at high supersaturations the Frenkel'–Courtney equation is better. The introduction of the Courtney correction $1/S$ would also improve the agreement with theory in Stachorska's experiments, particularly at higher supersaturations, where this correction is greater. The results of the comparison of theory and experiment are given in Fig. 1.

Edwards and Woodbury[155] studied nucleus formation in supersaturated ^4He vapour. Since their experiments were carried out at absolute temperatures of several degrees,

it may be assumed that heterogeneous formation of nuclei did not take place, since at such low temperatures, no substance is capable of generating condensation nuclei. Edwards and Woodbury found that the rate of nucleation is greater by several orders of magnitude than that predicted by the classical theory, and depends to a marked extent on the supersaturation. The number of particles formed in these experiments was very large, and this made it impossible to attribute the results to condensation on ions which might have remained in the chamber after the application of the electric field. This discrepancy is possibly due to anomalous physical properties in liquid helium.



Theoretical and experimental data on the dependence of the rate of nucleus formation in cm^{-3} s^{-1} on the supersaturation for water vapour in an atmosphere of helium at −5°C from various papers. Theoretical curves: A,[143] B,[1] C,[4] D,[68] E,[3] F,[2] and G,[66]. Experimental data: H[152] and solid circles[151].

In the calculation of the rate of nucleation in the works cited, the values of the surface tension for a flat liquid surface were assumed. Pound and La Mer[156] and Byers and Chary[157] compared experimental results with the calculation of $J(S)$ with allowance for the relationship $\sigma(r)$ found by Tolman, and found that the agreement between theory and experiment is lower when allowance is made for this relationship.

Nucleation under non-steady-state conditions was studied by Allard and Kassner[151] using a Wilson chamber with two-stage expansion. The second, slow stage of the expansion was carried out in order to compensate for the increase in temperature resulting from heat exchange. This precaution was necessary, since the duration of the condensation in their experiments was greater than usual. The number of drops formed was recorded by fast cinematography. According to Allard and Kassner[151], the rate of increase in J shows satisfactory agreement with Courtney's calculations[71], but as the vapour is exhausted the rate of decrease in J is less than that given by the calculations. A number of papers[138,139,143] describe the study of the formation of ice crystals in supersaturated water vapour at low temperatures. The formation of the ice crystals was detected from the freezing of supercooled sugar solution placed in the Wilson chamber. The freezing of the solution is initiated by ice crystals deposited from the chamber. Although in the works cited the formation of ice crystals was detected at temperatures below the range between −40° and −65°C, Mason and Maybank[158] and Mason[137] point out that there is no proof that the crystals were formed from the vapour, and not by the crystallisation of nuclei of supercooled liquid. Changes in the mechanism of the formation of nuclei could not be detected[139] in butanol vapour at temperatures as low as −75°C.

Flood[159] studied nucleation in a binary mixture of water and C_2H_5OH vapours and obtained good agreement with the theory of Neumann and Doring[68], but Flood's experiments[159] suffered from all the unsatisfactory features characteristic of early work with the Wilson chamber, so that it must be accepted that further study of nucleus formation in binary mixtures is required.

In concluding the examination of results obtained using the Wilson chamber, it may be noted that work carried out in recent years provides quantitative confirmation of the correctness of the classical theory, and of all the equations, Frenkel's equation with Courtney's correction is satisfied with greatest accuracy.

Recently, the study of condensation in supersonic aerodynamic nozzles has acquired considerable importance. Here, as in the Wilson chamber, supersaturation is established by adiabatic cooling. For all substances except helium, the decrease in the equilibrium vapour pressure due to the decrease in temperature on adiabatic cooling takes place more rapidly than the decrease in the static pressure, so that sufficiently great isoentropic expansion of the vapour–gas mixture or even the pure gas may lead to the production of high supersaturations. If the flow of the stream in a Laval nozzle is not accompanied by condensation, the change in the static pressure (that is the pressure which can be measured by an instrument moving with the stream) is described by the equation for an adiabatic process. The condensation of vapour leads to a sudden increase in pressure, proportional to the mass of the condensed substance, relative to the "dry" isoentropy, and an increase in temperature as a result of the liberation of the heat of condensation. Experimental methods for studying condensation in Laval nozzles are based on measurement of the distribution of the static pressure and temperature along the axis and comparison of the results obtained with the "dry" isoentropy. The magnitude of the deviation of the pressure from the dry isoentropy can be calculated by one of the methods mentioned in section III, and the comparison of the calculated and experimental values forms the basis of methods for verifying theories of condensation. Thus comparison of theory and experiment in this instance is carried out indirectly. Detection of fog formation by optical methods is also used, but since the droplets begin to produce appreciable light scattering only when they reach dimensions of 10^{-6} cm, the formation of the fog is detected with a slight delay, which may amount to 10^{-4} s. This last feature, which is not taken into account, has in turn been responsible for the erroneous opinion that a long time interval is required for the attainment of the steady state in nucleation[160].

Oswatitsch[111] showed that the experimental data of Binnie and Woods[161] and Yellot[162] on the condensation of water vapour can be correctly approximated by the results of theoretical calculations with appropriate selection of the values for the surface tension of water. Gyarmathy and Meyer[163] obtained quantitative agreement between their own analytical calculations based on Frenkel's equation

and experiments on the condensation of sodium and water vapours. Wegener and Pouring[164] established that the results of the study of the condensation of water vapour can be approximated by any of the equations of Frenkel', Yang, Becker and Doring, or Barnard, with the selection of appropriate values for the accommodation coefficient.

A number of papers have described the study of the condensation of nitrogen in Laval nozzles. Comparison of the results of this work with calculations is made difficult by the absence in this instance of a noncondensing gas, so that the heating of the growing particles by the heat of condensation cannot be neglected. Moreover, in the presence of various impurities, such as CO_2 and H_2O, heterogeneous condensation in fact take place[165,166], since the impurities, which condense before the start of the condensation of nitrogen, form condensation nuclei. Thus only the experiments on the condensation of pure dry nitrogen are of interest. Studies of this kind carried out by various authors have given results which show good agreement with one another[167,168]. Some of these data were compared by Griffin and Sherman[169] with the results of a stepwise calculation of condensation using Courtney's equation[16] and were found to show good agreement with these calculations. Quantitative comparison of theoretical calculations with the results of experiments in Laval nozzles leads to the conclusion that the discrepancy does not exceed the error in the calculations and the error in the measurements, which are fairly high. Qualitative agreement between experimental and calculated data was obtained by Norgen[170,171] who collected particles of aluminium and mercury chlorides formed by condensation of the corresponding vapours in a laval nozzle and studied them on an electron microscope. Thomann[172,173] found that crystals of ice with dimensions ~ 14 Å are formed by condensation of water vapour in a supersonic jet.

In addition to condensation in aerodynamic tubes, which have been studied by a number of workers[161-173], condensation in gas streams flowing through a nozzle with small diameter into a high vacuum has been studied intensively in recent years. By using a nozzle cooled with liquid helium it is possible to obtain streams with Mach numbers of up to 100 and a temperature of the order of several degrees Kelvin. An apparatus of this kind has been described in detail by Kantrowitz and Grey[174], and by Becker, Klingerhofer, and Lohse[175]. The flow of H_2, N_2, and He at a pressure of ~ 600 mmHg into a vacuum of ~ 10^{-5} mmHg has been studied[175]. The density of the flowing beams was varied in the range 10^{15}–10^{19} molecules cm^{-2} s^{-1}. It was established that the addition of another gas which does not condense under the conditions of flow to the gas condensing in the nozzle increases by a large factor the mass consumption of the condensing gas on passing through the nozzle. Thus dilution of N_2 with four times its volume of H_2 increased the density of the stream by a factor of 30. The addition of the noncondensing gas evidently facilitates condensation to the extent that it facilitates dissipation of the heat of association. The time required for attainment of the steady state was also estimated, and it was found that its order of magnitude agrees with that predicted by theory.

Henkes[176] used a mass spectrometer to detect the formation of aggregates in the apparatus of Becker, Klingerhofer, and Lohse[175]. He was able to detect aggregates containing up to 550 molecules in an H_2 stream. At the same time he established that the intensity of the electron beam bombarding the molecular beam being studied influences the distribution of the concentration of aggregates in the latter. Leckenby and coworkers[177] passes various gases and gas mixtures from a high-pressure cylinder into a mass spectrometer chamber through a nozzle with diameter 10^{-3} mm and established that aggregates of molecules are formed. When gas mixtures were used, the aggregates also consisted of different molecules. The concentration of aggregates was comparable with the concentration of monomeric molecules. An interesting feature is that for water vapour, aggregates with an even number of molecules were formed in larger quantities than the aggregates with an odd number of molecules. Greene and Milne[178] showed that the addition of 2.5% CO_2 to argon being passed through a nozzle into a mass spectrometer increases the ratio of the concentrations of monomer and dimer in argon by a factor of 3. The authors considered that this proves that the formation of the complexes is not due to the action of the ion source.

The determination of the concentration of aggregates in gases, even when these are not under supersaturation conditions, is of considerable interest for the verification of work on the calculation of the equilibrium concentrations of small aggregates. Bentley[179] used a combination of mass spectrometry and the Kundsen effusion technique to measure the concentration of associates of molecules in CO_2. He showed that the concentrations of the associates are given by power functions of the concentration of the monomer. In particular, he found that $C_2 \sim C_1$,[2,85] $C_3 \sim C_1$,[7,8] and $C_4 \sim C_1$.[11] Bentley showed that CO_2 contains aggregates of up to 23 molecules.

It has not as yet been possible to interpret quantitatively the results of mass spectrometric studies of the formation of nuclei. The attempt made by Dunning[180] cannot be regarded as successful, since he used macroscopic values of the surface tension and density in the calculation of the equilibrium concentrations of these small clusters.

Milne[181] compared the results of mass spectrometric determinations of the formation of dimers during the flow of argon through a molecular nozzle with calculations by the method of Storgyn and Hirshfelder[96] and obtained satisfactory agreement.

Spontaneous condensation during the cooling of a vapour–gas stream in a heat exchanger with turbulent flow was the subject of a theoretical and experimental study by Amelin[118,182]. An ultramicroscope was used to determine the mean dimensions and concentration of droplets of sulphuric acid and glycerol, and the results were compared with those obtained by a theoretical stepwise calculation. It was shown that when Frenkel''s equation is used, satisfactory agreement with experiment is obtained for glycerol, the experimental and theoretical values of the count concentration differing by a factor of not more than 3–4. For sulphuric acid, however, the results of calculations using the Becker–Doring equation gave better agreement with experiment.

A third method for achieving supersaturation in experiments on spontaneous condensation is by mixing streams of gases at different temperatures, with the hotter gas containing the condensing vapour, or by mixing hot vapour with a cold gas by molecular diffusion.

Spontaneous condensation during the mixing of streams at different temperatures was first studied by Fuks and Oschmann[183] and by Petryanov and Tunitskii[127], who used three-way capillaries for the mixing. The inadequate state of development of the theory of turbulent mixing at that time made it impossible to carry out a quantitative interpretation of the results obtained. Some important qualitative conclusions were reached in this work, however. In particular, it was concluded that with increase in the concentration of condensing vapour the rate of nucleus

formation does not increase indefinitely, but reaches a limiting value. Petryanov and Tunitskii[127] also concluded that in the condensation of the vapour of substances with low volatility and very low partial pressures, the formation of aerosols takes place by a coagulation mechanism. This is not always true, however, since Fuks and Sutugin[184], in a study of the condensation of NaCl vapour with a partial pressure of $\sim 10^{-7}$ mmHg, showed that when streams at different temperatures are mixed in a three-way tube, the concentration of the aerosol formed may be very low— $\sim 10^2$ cm^{-3}—and this excludes the possibility of a coagulation mechanism.

An elegant method for studying spontaneous condensation using an immersed turbulent stream was proposed by Amelin[185]. The method is based on the fact that the supersaturation in the mixing zone of the stream at first increases with dilution of the hot gas of the stream, reaches a maximum, and then decreases. By varying the temperature of the flowing stream and the medium, it is possible to achieve conditions under which the supersaturation will exceed the critical value only in a very narrow part of the mixing zone. The critical supersaturation of glycerol vapour[186] determined by this method was found to be close to that calculated by the Volmer–Flood formula. Higuchi and O'Konski[123], using an improved version of Amelin's method, showed that Frenkel's equation very effectively describes nucleation in dibutyl phthalate and glycerol vapours but describes that in sulphur vapour slightly less effectively. The agreement for triethylene glycol was poor, and the authors cited attributed this to the presence of impurities. It should be noted that in their comparison of experiment and theory, Higuchi and O'Konski compared the published values of the surface tension of the substances used with values calculated from experimental data on the rate of nucleation. Since J depends to a very marked extent on σ, there may be considerable discrepancy in J for good agreement in the values of σ. Sutugin and Fuchs[73] studied the condensation of silver vapour in a hot submerged stream of argon. They deposited the aerosols obtained, measured the weight of the deposit and its specific surface, and used these results to calculate the dimensions of the particles and their count concentration. The experimental results were compared with theoretical calculations carried out by means of a theoretical scheme which they developed, using Reed's method[44] to calculate the free energy of the nuclei and the Rosinski–Snow scheme[131] to calculate the coagulation growth of the particles. The partial pressure of silver vapour in these experiments amounted to 0.01–1 mmHg. The nuclei began to be formed in significant quantities at supersaturations of $\sim 10^5$. It was shown that the degree of dispersion of the aerosols formed at high supersaturations is determined by coagulation, accompanied by merging of the particles. It was also shown that the proposed scheme of calculation can be used to predict quantitatively the parameters of the aerosols formed.

Spontaneous condensation during the mixing of coaxial streams at different temperatures in the diffuser of a KUST instrument[187] was studied by Kogan[188] and Rybin[189]. Kogan[188] showed that the introduction of the molecules of various substances decreases the magnitude of the critical supersaturation in diiso-octyl sebacate vapour, in qualitative agreement with Neumann and Doring's conclusion that in binary mixtures the critical supersaturation should be different from that in the pure vapours of each component. Rybin[189] studied the spontaneous condensation of the vapours of a number of organic liquids with low volatility in a KUST instrument. By making use of the equations for the material and heat balances, he calculated the magnitude of the supersaturation achieved with complete mixing of the streams, assuming that mixing precedes nucleus formation, and neglecting the condensation of vapour on the walls during mixing. The values of J calculated from the equations of the classical theory were found to be smaller than the experimental values by several orders of magnitude.

Gen and coworkers[190] studied aerosols formed by the diffusion of aluminium vapour into a cold rarefied inert gas. It was found that the dimensions of the particles decrease rapidly at first with decrease in the concentration of the vapour, and then remain almost unchanged, that is the concentration of the particles at first increased, and then reached a limiting value. The concentration of particles for a given concentration of vapour increased with decrease in the pressure of the inert gas. Turkevitch[191] used an analogous method to study the condensation of silver vapour and showed that the degree of dispersion of the resulting aerosol is determined by coagulation. The increase in concentration with decrease in the pressure of the inert gas was attributed to an increase in the rate of diffusion of the vapour and hence an increase in the rate of cooling.

Higuchi and O'Konski[123] pointed out that it is possible to achieve supersaturation by chemical or photochemical reactions. It has not yet been possible, however, to find a reaction which would take place so rapidly that it would be complete before the start of condensation of the product. In the large number of experiments on the study of condensation with chemical reaction, the latter took place at the same time as nucleation, and the reaction was usually catalysed on the surface of the forming particles. These features make quantitative interpretation of the experiments difficult.

In summarising the examination of the results of the experimental study of spontaneous condensation, it must be accepted that the experimental data confirm the classical Volmer–Frenkel–Becker–Doring–Zel'dovich theory rather than the new Lothe–Pound–Hirth theory. It can also be stated that existing methods for calculating the processes of aerosol formation using the equations of the theory of spontaneous nucleus formation make it possible to predict the parameters of the resulting aerosols with sufficient accuracy for practical purposes.

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Karpov Physicochemical
Institute, Moscow

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The Problem of Monatomic Multicharged Ions and the Nature of the Chemical Bond in Inorganic Crystals

A.A.Levin, Ya.K.Syrkin, and M.E.Dyatkina

The review deals with the problem of the chemical bond in inorganic solids on the basis of the analysis of the experimental data. It is shown that thermochemical and crystal-chemical arguments can hardly be regarded as proof of the ionic theory, while data derived by modern methods for the direct estimate of effective charges show quite definitely that the bonds are covalent even in structures such as alkaline earth metal oxides and chalcogenides. The bibliography comprises 116 references.

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I. INTRODUCTION

The aim of the present review is to examine the present state of the problem of the nature of the chemical bond in inorganic crystals. Although the concept of the partial covalence of such crystals has now become fairly widespread[1-3], the tendency to regard this "covalent component" as a relatively small correction to the ionic state predominates. One of the reasons for this situation is the traditional belief that the classical ionic theory and its concepts of multicharged ions are consistent with the majority of thermochemical and crystal-chemical data, which are thus regarded as "proof" of the validity of this theory. More detailed analysis shows, however, that in all cases, except alkali metal halides, thermochemical and crystal-chemical arguments are not convincing and in fact it is not experimental data that are consistent with the ionic theory but certain theoretical postulates in the thermochemistry of crystal lattices and in crystal chemistry—branches of science which have developed for half a century under the dominant influence of the ionic concept. Therefore such agreement is not surprising, but, rather than being the foundation of the ionic model, it is its consequence. The relevant questions have been examined in sections II and III of the present review.

On the other hand a fairly large amount of direct experimental data on charge distribution in inorganic solids has now accumulated. These experimental results show that the only inorganic crystalline materials close to a purely ionic state are probably alkali metal halides, for which the ionic theory holds almost completely. In crystals of compounds of "polyvalent" elements the effective charges do not increase but are actually more likely to decrease with increase in formal valence. Thus the effective ionic charges in alkaline earth metal oxides and chalcogenides ($A^{II}B^{VI}$) do not exceed unity in all probability† and in compounds of the type $A^{III}B^{V}$ they are approximately 0.5. In

† However, many workers continue to regard these crystals as purely ionic[4].

compounds more complex than the binary compounds with the composition AB the situation is somewhat more complicated but even in crystals of this kind the effective ionic charges are low‡. Experiments show that the anionic charges never exceed about 1 e, while cationic charges may be somewhat greater. Experimental data on the effective charges are considered in section IV.

The review concludes with section V, where the question of the possible physical cause limiting the effective charge of the atom in a molecule or crystal is discussed. The concluding paragraph deals with the problem of the quantum-mechanical description of the partially covalent state in solids. A fairly typical example, showing how an appreciable departure from a purely ionic structure can lead to a considerable change in the physical properties of the solid, is also quoted there.

II. THERMOCHEMICAL DATA AND THE PROBLEM OF MULTICHARGED IONS

The fundamental thermochemical concept in ionic theory is the so called "lattice energy" (Table 1), i.e. the energy which would be evolved in a hypothetical process involving the mutual approach of ions (including multicharged ions) from infinity to real atomic distances in the crystal. Two properties are then used as the main evidence in favour of the ionic model (Table 1): (1) the similarity of the "theoretical" and "experimental" lattice energies; (2) the sharp increase in lattice energy on going from compounds of "univalent" elements to compounds of "polyvalent" elements, in full agreement with the quadratic relation between the energy of electrostatic attraction and the charge.

Table 1. Theoretical (U_T) and experimental (U_E) lattice energies in crystals*

Crystal	U_T, kcal mole^{-1}	U_E, kcal mole^{-1}	Q, kcal mole^{-1}	E_{atom}, kcal mole^{-1}
NaF	217 [5]	217 [7]	136	180
KF	193 [5]	193 [7]	134	174
RbF	184 [5]	185 [7]	131	170
CsF	176 [5]	173 [7]	127	164
NaCl	185 [5]	185 [7]	98	152
KCl	168 [5]	169 [7]	104	154
RbCl	161 [5]	162 [7]	103	152
MgO	942 [6]	942 [6]	144	239
CaO	865 [6]	853 [6]	152	257
SrO			141	239
BaO	756 [6]	766 [6]	133	235
MgS	807 [6]		83	178
CaS	740 [6]		115	220
SrS	696 [6]		108	200

* The heats of formation (Q) of the compounds and the heats of sublimation of the metals taken from Ref. 8 and the dissociation energies of diatomic molecules taken from the summarising table in Ref. 16 were used to calculate the atomisation energy E_{atom}. Here and henceforth literature references are quoted immediately after the numerical data.

‡ It is superfluous to emphasise that the concept of the essentially covalent structure of inorganic crystals in no way contradicts the generally known experimental facts, for example, Faraday's laws of electrolysis. Furthermore, in solutions we are dealing not with atomic but with solvated ions.

However, simple analysis shows that for compounds of "polyvalent" elements both these properties do not reflect any experimental relations but are a consequence of the definition of the concept of the "theoretical" lattice energy, which is calculated precisely on the basis of the postulate of the ionic nature of the bond.

1. Theoretical Lattice Energy

The theoretical lattice energy U_T is by definition a purely computational quantity which can be formally calculated for any system of real or fictitious charges. Nevertheless the use of this concept in the theory of crystal lattices already involves certain difficulties.

Even within the framework of the postulated ionic model U_T cannot be calculated unambiguously, since in the expression for the theoretical lattice energy§

$$U_T = \frac{MZ^2}{R} - U_{rep.}, \qquad (1)$$

the electrostatic bond mechanism defines only the first term $U_{electr} = MZ^2/R$. The exact form of the second term U_{rep} is unknown (it is specified by the expression for the potential V_{rep}, which takes into account the repulsion between ions at distances smaller than the equilibrium value). Usually any one of the model functions of the following types is employed for the "repulsion" potential:

$$\begin{aligned} &\text{(a) } V_{rep.} = br^{-n} && \text{Born and Lande [9]},\\ &\text{(b) } V_{rep.} = be^{-ar} && \text{Born and Mayer [10]},\\ &\text{(c) } V_{rep.} = \varepsilon + be^{-ar} + cr^{-6} + dr^{-8} && \text{Ladd and Lee [11]}, \end{aligned} \qquad (2)$$

but none of these has a rigorous theoretical foundation and therefore none has any advantages over the others¶. However, the use of different functions (and different parameters a, b, and c, ...) leads to appreciable discrepancies in the corresponding values of U_T (Table 2). This discrepancy amounts to only 1–2 kcal mole^{-1} for alkali metal halides, but increases by a factor of several tens for other compounds.

Table 2. Theoretical lattice energy U_T of crystals according to different calculations

Crystal	Na_2O	K_2O	Rb_2O	MgO	CaO	BaO	ZnO	GeO_2	SnO_2	TiO_2
U_T, kcal mole^{-1}	651 [5]	580 [5]	552 [5]	942 [6]	865 [6]	756 [6]	990 [15]	2534 [18]	2301 [18]	2429 [18]
	600 [17]	529 [17]	508 [19]	907 *	816 *	726 *	917 [19]	3210 [19]	2845 [19]	2958 [19]

* From Ref. 32, Vol. I; according to Baughan's data [14].

§ Here Z is the formal ionic charge, R the anion–cation interatomic distance, and M the Madelung constant, which is 1.64 for a ZnS type lattice and 1.75 for an NaCl type lattice. Eqn. (1) is written in terms of atomic units.

¶ Sometimes it is suggested that Eqn. (b) follows from quantum mechanics and therefore is more justified, than, for example, Eqn. (a). In fact Eqn. (b) is a simplified version of the formula obtained by Unsöld [12] and Brück [13] for the repulsion potential between a positive point charge and a hydrogen-like atom and cannot be applied to real crystals.

The attempts to calculate U_T for the ionic model by the more correct quantum-mechanical procedure also proved to be comparatively successful only for alkali metal halides [20-23]. The results of the calculation [24] for MgO by the same method [20-23] using Watson's functions [25] for O^{2-} ions agree with elementary electrostatic calculations (Tables 1 and 2) only to a first approximation: $U_T^{(1)} = 923$ kcal mole^{-1} and the equilibrium lattice constant $a^{(1)} = 4.23$ Å. In calculations based on a second approximation it was found unexpectedly that the mutual repulsion of ions, which had always been neglected, exceeds in fact by a factor of 2-3 (!) the Born repulsion between anions and cations, so that the more accurate calculation leads to much poorer results: $U_T^{(2)} = 747$ kcal mole^{-1} and the lattice constant $a^{(2)} = 5.5$ Å (against the experimental value $a = 4.21$ Å)†.

2. Experimental Lattice Energy

In the discussion of experimental lattice energies, U_E it is necessary to consider two cases which differ sharply in their physical significance. For compounds of "univalent" elements, U_E is determined with the aid of the Born-Haber cycle from the equation

$$U_э = Q + S + \tfrac{1}{2}D + I_1 - F_1 \qquad (3)$$

where Q is the heat of formation of the compound AB, S the heat of sublimation of the metal A, D the heat of dissociation of the molecule B_2, I_1 the first ionisation potential of the metal A atom, and F_1 the affinity of the non-metal B atom for one electron. For compounds $A^{I}B^{VII}$, all the quantities on the right-hand side of Eqn. (3) are susceptible to direct experimental determination regardless of any hypotheses concerning the nature of the bond between the atoms in the crystal. Thus the heats Q, S, and D and I_1 are obtained by direct thermochemical and spectroscopic measurements [26,27], and the affinity for one electron F_1 can be determined, for example, from data on light-induced ejection of an electron [28]. Therefore in the case of alkali metal halides U_E is a purely experimental quantity and the agreement between U_T and U_E indeed means that the corresponding crystals can be regarded as constructed from the ions Li^+, Na^+, ..., F^-, Cl^-, ...

The situation is quite different for compounds of "polyvalent" elements for example the oxides and chalcogenides of alkaline earth metals or transition metals: Mg, Ca, Ti, V, etc. In this case the "experimental" lattice energy is defined thus:

$$U_E = Q + S + \tfrac{1}{2}D + I_1 + I_2 - F_1 - F_2 \ . \qquad (4)$$

At first sight this expression is constructed in the same way as that for univalent elements. However, in fact there is a profound difference between Eqns. (3) and (4).

† It is remarkable that when account was taken of the repulsion between anions in the calculation of Peterson et al. [23] for sodium chloride, poor agreement between the values of U_T and U_E was again obtained. Thus the calculation to first-order approximation gave $U_T^{(1)}$ (NaCl) = 183 kcal mole^{-1} and $A^{(1)} = 5.4$ Å, while the calculation to second-order approximation (taking into account the repulsion between Cl^- ions) gave $U_T^{(2)}$ (NaCl) = 155 kcal mole^{-1} and $a^{(2)} = 6.77$ Å.

The quantity U_E calculated from Eqn. (4) cannot be regarded as the result of an experimental (if only in principle) Born-Haber cycle, i.e. as a physical quantity susceptible to experimental measurements, since Eqn. (4) includes together with experimentally measured quantities Q, S, D, I_1, I_2, and F_1 also a quantity of a significantly different type. This quantity is the affinity of the atom for a second electron (F_2), which cannot be found by any independent method.

3. Affinity of the Atom for Several Electrons

The reason why F_2 cannot be determined is due to the fact that the affinity for a second electron would have to be understood as the energy of the process

$$B^- + e^- \rightarrow B^{2-} + F_2 \qquad (5)$$

which in reality never takes place‡. The experimental data show that for free atoms such a process cannot in fact occur since the binding energy of even one "superfluous" electron in the singly charged ions O^-, S^-, etc. is low (see section V, 1). On the other hand, there are no direct experimental data which would indicate the existence of monatomic multicharged negative ions in molecules or crystals (see section IV) and theoretical considerations also cast doubt on their existence (see section V).

It is noteworthy that although the concept of affinity for several electrons is usually associated with the thermochemistry of crystal lattices, real thermochemical data by themselves, without the previously adopted ionic concept, do not require the introduction of such a concept at all. The heats of formation and atomisation energies of alkali metal halides and alkaline earth metal oxides and chalcogenides are compared in Table 1. It is evident from this table that the heats of formation of the chalcogenides are close to the heats of formation of the halides and are in no way comparable to the enormous "lattice energies" for doubly charged ions§. Thus the only reason for the introduction of the concept of affinity for several electrons was the attempt to compensate the excessively large attraction energy of multicharged ions in the ionic model, i.e. essentially to adjust the experimental heats of formation to the postulates of the ionic theory (very large negative values must be attributed to the affinity for several electrons [32]).

4. The Reason for the Agreement Between the "Experimental" and "Theoretical" Lattice Energies

The vicious circle indicated above makes it impossible to find U_{exp} by an experimental procedure even within the framework of the ionic model. In order to escape from this vicious circle, it is usually postulated in the ionic

‡ From the standpoint of quantum mechanics, extremely unstable doubly charged ions with a lifetime of the order of 10^{-10} s are possible [29]. According to some data, such ions (with a lifetime of about 10^{-4} s) were recently observed mass-spectrometrically [30], although in another paper [31] doubt was cast on these results. At any rate the presence of such unstable species in no way supports the ionic theory, particularly since doubly charged ions F^{2-}, Cl^{2-}, and Br^{2-} with the same lifetime were observed together with O^{2-} in this investigation [30].

§ The difference between the atomisation energies is of course greater. However, it too is insignificant compared with the difference between the lattice energies.

theory that crystals have a purely ionic structure, and that in Eqn. (4) for any one compound adopted as a standard it is possible to substitute U_T for U_E. Then the corresponding "affinity for two electrons":

$$F_1^0 + F_2^0 = Q^0 + S^0 + \frac{1}{2}D + I_1^0 + I_2^0 - U_T^0 \qquad (6)$$

is adopted as the "experimental" value and is substituted in Born's cycle [formula (4)] for all other compounds. However, it is readily seen that U_E is then given by the equation

$$U_E = U_T^0 + (Q - Q^0) + (S - S^0) + (I_1 + I_2 - I_1^0 - I_2^0) = \qquad (7)$$
$$= U_T + (U_T^0 - U_T) + (Q - Q^0) + (S - S^0) + (I_1 + I_2 - I_1^0 - I_2^0) = U_T + \Delta U ,$$

where the sum of the quantities in brackets (ΔU) is small compared with the first term U_T¶. Thus Eqn. (7) shows that the so called "experimental" lattice energy U_E represents essentially the same "theoretical" energy U_T after it has been only slightly modified by experimental data. Therefore neither the order of magnitude of U_E nor the agreement between U_T and U_E reflect any experimental facts and of course cannot be regarded as proof of the ionic structure of the corresponding crystals.

Although Eqn. (7) makes it possible to explain in broad outline both the order of magnitude of U_E and the approximate agreement between U_E and U_T, it is frequently asserted that the "thermochemical" affinities for several electrons obtained for different lattices are so close that it is bound to imply the reality of multicharged ions. Therefore we shall consider the question of this agreement in detail (for oxygen as an example). In the first place, as shown by Eqn. (6), the quantity $F_1 + F_2$ is not purely experimental but depends on the value of U_T. Therefore, even for the same compound, $F_1 + F_2$ may assume different values depending on which formula is selected for the calculation of U_T. For example, the values of $F_1 + F_2$ for CaO calculated using the theoretical lattice energy[6] U_T(CaO) = 865 kcal mole^{-1} [6] (the Ladd–Lee formula) and the value[14] U_T(CaO) = 816 kcal mole^{-1} (the Born–Meyer formula) are respectively about −190 and about −140 kcal mole^{-1}, i.e. differ by 50 kcal mole^{-1}. A similar discrepancy is found when the same formula is used for different compounds, even when these are of the same structural type. Thus when the Born–Lande formula is applied to CaO, we have U_T = 852 kcal mole^{-1} [15,32] and then $F_1 + F_2$ = −177 kcal mole^{-1}, while for VO we have U_T = 996 kcal mole^{-1} [15,32] and $F_1 + F_2$ = (−220)–(−240) kcal mole^{-1} (the heat of formation of VO has evidently not been established exactly[33]). Consequently the "thermochemical" affinity of oxygen for two electrons can vary within extremely wide limits, from 140–150 kcal mole^{-1} [17,32] to 220–240 kcal mole^{-1} and therefore one can speak of the constancy of this affinity to within 10–15 kcal mole^{-1} only in a very restricted sense for a series of chemically and crystal-chemically similar compounds and under the condition that the same formula is used to calculate U_T.

However, in this case the constancy of the right-hand side of Eqn. (6) is not surprising. It is accounted for simply by the fact that in a series of such compounds the potentials I_1 and I_2 vary in parallel with $1/R_{cation} \propto 1/R \propto U_T$, whereas the heats Q vary within comparatively narrow limits (see, for example, Table 1).

¶ $Q - Q^0$ and $S - S^0$ are usually small (for alkaline earth metal oxides each of these does not exceed about 10 kcal mole^{-1}) and the quantities $U_T^0 - U_T$ and $I_1 + I - I_1^0 - I_2^0$ usually have different signs and cancel out.

5. "Thermochemical" and "Spectroscopic" Affinities for Several Electrons

The agreement between the "thermochemical" affinity for two electrons and the corresponding "spectroscopic" value is sometimes quoted as yet another argument in favour of the ionic theory. The "spectroscopic" value of F_2 is understood as the quantity found by the extrapolation of the spectroscopic values of the ionisation potentials and affinities for one electron and hence independent of lattice energy. However, such arguments, based on the "agreement" between $(F_2)_{thermochem}$ and $(F_2)_{spectr}$ can also be scarcely regarded as convincing. Indeed the "spectroscopic" value of F_2 as well as the "thermochemical" value are not constant but depend on the method of extrapolation. Thus extrapolation for the isoelectronic series from F^- to S^{6+} yields $F_1 + F_2$ = −155 kcal mole^{-1} for the oxygen atom[34]; Glockler's formula[35] $J = \alpha z^2 + \beta z + \gamma$ yields $F_2 \simeq$ −191 kcal mole^{-1},[36] while according to the data of Crossley and Coulson[37], the "spectroscopic" affinity of oxygen for two electrons is estimated as −118.6 kcal mole^{-1}. Since F_1 ranges from 23.5 to 46 kcal mole^{-1} according to different estimates (see Ref. 32, Vol. II), it follows that $(F_2)_{spectr}$ varies in the range 140–200 kcal mole^{-1} and the agreement of this value with $(F_2)_{thermochem}$, which varies in the range 140–220 (240) kcal mole^{-1} can be treated only as agreement with respect to the order of magnitude.

Finally, one must bear in mind that ionisation potentials and affinities for one electron correspond to bound states of the electron in the atom which are physically completely different from the free state corresponding to the hypothetical multicharged ion. From this standpoint, the extrapolation procedure itself for the determination of $(F_2)_{spectr}$ appears altogether fairly doubtful. On the other hand, if one assumes, in accordance with the ionic theory, that the structure of the energy levels of the atom in a compound changes radically, the multicharged ion passing into a bound state, then the use of the energy levels of the free atom in the extrapolation does not appear very logical.

Table 3. Comparison of the theoretical and experimental lattice energies for various crystals

Crystal	U_T, kcal mole^{-1}	U_E, kcal mole^{-1}	Q, kcal mole^{-1}	E_{atom}, kcal mole^{-1}	Crystal	U_T, kcal mole^{-1}	U_E, kcal mole^{-1}	Q, kcal mole^{-1}	E_{atom}, kcal mole^{-1}
ZnO	917	981	83	173	Cu_2O	656	794	40	262
ZnS	794	878	48	133	Cu_2S	555	706	19	235
ZnSe	753	864	34	114	Ag_2O	619	730	7	205
CdO	854	921	61	137	Ag_2S	528	663	8	199
CdS	746	827	34	105	Ag_2Se	518	658	3	189
HgO	828	944	22	96	Tl_2O	552	646	42	187
HgS	726	869	13–14	82	Tl_2S	491	557	21	160
HgSe	692	860	5	85	Tl_2Se	470	554	18	153
SnO	815	883	68	138	SiO_2	3280	3137	205	429
SnS	712	765	19	144	GeO_2	3210	3066	128	321
PbO	777	852	52	158	SnO_2	2301 [18]	2924 [18]	139	329
PbS	686	754	22	122	TiO_2	2429 [18]	2900 [18]	218	448
PbSe	655	750	18	115	MnO_2	3100 [40]	3670 [40]	124	311

* All the values of U_T and U_E, with the exception of those given individual references, were taken from Yatsimirskii[19]. The heats of formation Q of the compounds and the heats of sublimation of the metals were taken from Ref. 8; the heats of formation of silicon, germanium, and tin compounds were taken from Benson[39].

6. Thermochemical Arguments Against the Ionic Theory

As shown in subsections 3 and 5 in section II (mainly for alkaline earth metal oxides), thermochemical data can never be treated as proof of the ionic theory. For other compounds, the discrepancies between the thermochemical data and the predictions of the ionic model become so large† that they in fact turn into direct arguments against this model.

The theoretical and experimental lattice energies of a number of substances are compared in Table 3. The discrepancy between U_T and U_E reaches in this case an amount equal to the heat of formation of the compounds (or the affinity of the anions for two electrons, if this is preferable) and sometimes actually exceeds it. Evidently, in such a case one is dealing with a sharp discrepancy between experiment and the ionic model.

III. IONIC RADII AND CRYSTAL CHEMISTRY

Classical crystal chemistry with its central concept of ionic radius has always been regarded as closely related to the ionic model; therefore crystal-chemical arguments are usually advanced in favour of this model (see Ref. 41 for example). Three such arguments are most often discussed.

1. The possibility of employing ionic radii, including the radii of multicharged ions, to represent interatomic distances. [If the ions Mg^{2+} and O^{2-} do not exist, then why is $R(Mg^{2+}) + R(O^{2-}) = R(MgO)$?].

2. The relative dimensions of anions, cations, and neutral atoms. [The ionic radius of Mg^{2+} in the MgO structure is $R(Mg^{2+}) = 0.65$ Å and the atomic radius is $R(Mg) = 1.5$ Å; does this not demonstrate that all the valence electrons have been removed from the magnesium ion?].

3. The possibility of explaining the crystal structure on the basis of the Magnus–Goldschmidt "stability limits" [radius ratio rules (Ed. of Translation)]. (Geometry shows that precisely six spheres with a radius of 1.40 Å can be accomodated around a sphere with a radius of 0.65 Å. Does this not confirm that magnesium and oxygen ions in the MgO crystal are spheres with precisely this radius?).

We shall discuss these arguments in succession.

1. Anion–Cation Distances

The generally adopted ("classical") systems of ionic radii[42-50] are well known and agree with one another to within several hundredths of an ångstrom. One of these (Pauling's system) is quoted in the first column of Table 4. In any of these systems the sum of the radii $R(A^{n+}) + R(B^{n-})$ is equal to the interatomic distance and in this sense they all indeed "explain" the experimental data. The problem is, however, how unambiguously ionic radii may be obtained from experimental interatomic distances. We are restricting for the time being the discussion to anion–cation distances; it is easy to show that none of the "classical" scales does in fact follow from experimental data, since comparison of such interatomic distances can in general yield no information about the actual dimensions of the ions. The only experimental relation which follows from a comparison of interatomic distances is the approximate constancy of differences of the following type (Å):

$$\begin{aligned} &R(CaO) - R(MgO) = 0.30, \\ &R(CaS) - R(MgS) = 0.24, \\ &R(CaSe) - R(MgSe) = 0.23, \\ &\ldots\ldots\ldots\ldots \end{aligned} \tag{8}$$

or analogous differences for the same metal atoms (Å):

$$\begin{aligned} &R(MgS) - R(MgO) = 0.50, \\ &R(CaS) - R(CaO) = 0.44, \\ &R(SrS) - R(SrO) = 0.37, \\ &\ldots\ldots\ldots\ldots \end{aligned} \tag{9}$$

Table 4. Various systems of ionic radii (Å)

Pauling's ionic radii (Refs.47-49)		Slater's ionic radii (Refs.51 and 52)		Ionic radii from (Ref.53)		Ionic radii found by Pauling's rule [see (III),5)]	
Li^+	0.60	Li	1.45				
Na^+	0.95	Na	1.80				
K^+	1.33	K	2.20				
Rb^+	1.48	Rb	2.35				
Cs^+	1.69	Cs	2.60				
Be^{2+}	0.31	Be	1.05				
Mg^{2+}	0.65	Mg	1.50	Mg^+	1.35	Mg^+	1.25
Ca^{2+}	0.99	Ca	1.80	Ca^+	1.65	Ca^+	1.55
Sr^{2+}	1.13	Sr	2.00	Sr^+	1.82	Sr^+	1.62
Ba^{2+}	1.35	Ba	2.15	Ba^+	2.01	Ba^+	1.81
F^-	1.36	F	0.50				
Cl^-	1.81	Cl	1.00				
Br^-	1.95	Br	1.15				
I^-	2.16	I	1.40				
O^{2-}	1.40	O	0.60	O^-	0.75	O^-	0.88
S^{2-}	1.84	S	1.00	S^-	1.25	S^-	1.20
Se^{2-}	1.98	Se	1.15	Se^-	1.38	Se^-	1.35
Te^{2-}	2.21	Te	1.40	Te^-	1.40	Te^-	1.55

Eqns. (8) and (9) can perhaps be naturally interpreted as an indication of the approximate constancy of the "dimensions" of atoms—at least in a series of compounds similar in the chemical and crystal-chemical sense. However, even such an interpretation yields only the differences between the corresponding radii (Å):

$$\begin{aligned} &R(Ca) - R(Mg) = 0.23 - 0.30, \\ &\ldots\ldots\ldots \\ &R(S) - R(O) = 0.37 - 0.50 \\ &\ldots\ldots \end{aligned} \tag{10}$$

and not the true "dimensions" of atoms or ions‡. The position does not change when instead of similar compounds one considers compounds belonging to different types (both in the chemical and crystal-chemical sense). As in the previous case, it is readily seen, that a comparison, for example, of the equations (Å)

$$\begin{aligned} &R(Mg) + R(O) = 2.10 && (\text{in MgO}), \\ &R(Na) + R(O) = 2.41 && (\text{in } Na_2O), \\ &R(Mg) + R(F) = 1.98\text{–}2.05 && (\text{in } MgF_2), \\ &R(Na) + R(F) = 2.31 && (\text{in NaF}) \end{aligned} \tag{11}$$

† Provided, of course, that one considers real values and is not satisfied with agreement between the fictitious quantities U_T and U_E to within 15 or 20%! A typical example of such an error is the calculation of the bonding energies of the Mn^{2+} and O^{2-} ions in the MnO crystal[38]. The Heitler–London method yields in this case U_T = 796 kcal mole^{-1}, which is regarded as satisfactory because of the good agreement with U_E = 923 kcal mole^{-1}. In fact the actual accuracy of the calculation is much lower, since the "theoretical" and "experimental" heats of formation differ by a factor of two.

‡ Eqns. (10) show, incidentally, that the very concept of ionic radius is at best valid only to within 0.1 Å. Therefore there is hardly much point in specifying any system of ionic radii with undue precision.

yields nothing except the differences between the ionic radii (Å):

$$\begin{aligned} R(\mathrm{Na}) - R(\mathrm{Mg}) &= 0.31, \\ \cdots\cdots\cdots & \\ R(\mathrm{O}) - R(\mathrm{F}) &= 0.10, \\ \cdots\cdots\cdots & \end{aligned} \qquad (12)$$

although in this case for anions and cations of different valences.

The difficulty pointed out above is general, since any comparison of interatomic anion–cation distances defines the true dimensions of ions only to within an arbitrary constant, which can be added simultaneously to all anionic radii and subtracted from all cationic radii (or conversely). Therefore it is not surprising that, together with the "classical" systems of ionic radii, there may exist also other systems, which differ sharply from the former. One of such "non-classical" systems was recently developed by Slater [51,52] on the basis of calculations of atomic wave functions [54,55] by the Hartree–Fock method and was tested on more than 1200 interatomic distances. This scale restores to a certain extent the system of Bragg radii [56], proposed before the beginning of the "ionic period" in crystal chemistry, and differs from the "classical" scale in that the radii of anions are reduced and those of the cations increased by 0.85 Å. It is remarkable that, although Slater's radii apply not to ions but to neutral atoms, nevertheless with their aid the experimental interatomic distances are satisfactorily reproduced even for crystals such as alkali metal halides.

Table 5. Experimental [52] (in brackets)* interatomic distances and the radii of singly charged ions in $A^{II}B^{VI}$ crystals

$R(B^{1-})$	B^{1-}	$R(A^{1+})$			
		1.35	1.65	1.82	2.01
		A^{1+}			
		Mg^+	Ca^+	Sr^+	Ba^+
0.75	O^-	2.10* (2.10)	2.40* (2.40)	2.57* (2.57	2.76* (2.76)
1.25	S^-	2.60* (2.60)	2.90 (2.84)	3.07 (2.94)	3.26 (3.18)
1.38	Se^-	2.73* (2.73)	3.03 (2.96)	3.20 (3.12)	3.39 (3.31)
1.40	Te^-	2.75* (2.75) wurzite	3.05 (3.17)	3.22 (3.24)	3.41 (3.50)

* The upper number (without brackets) is the sum of ionic radii $R(A^+) + R(B^-)$. [53] The values denoted by an asterisk were used to calculate $R(A^+)$ and $R(B^-)$.

Another similar scale of ionic radii (corresponding to singly charged ions of the "divalent" elements Mg^+, Ca^+, ..., O^-, S^-, ...) was recently examined [53] in connection with the structure of the energy bands in crystals of compounds of the type $A^{II}B^{VI}$. These radii are listed in Table 5, which shows that they too give a good representation of interatomic distances, at least to within a reasonable accuracy of about 0.1 Å (see the footnote on p. 99).

2. Ionic Radii and Anion–Anion Distances

It may prove that the true dimensions of ions can still be derived from purely crystal-chemical data if, instead of anion–cation distances, one uses anion–anion distances and assumes that in certain structures anions can be in contact. Many years ago Lande postulated that such a case is realised in practice, for example in the structures of MgS and MnS and MgSe and MnSe, for which the interatomic distances are as follows (Å):

MgS	2.60	MnS	2.59
MgSe	2.73	MnSe	2.72 .

The approximate equality of the interatomic distances in the sulphides MgS and MnS and also in the selenides MgSe and MnSe enables Lande to assume [57] that the anions in these compounds touch one another and ultimately he obtained the following radii for the anions S^{2-} and Se^{2-}: $R(S^{2-}) = 1.83$ and $R(Se^{2-}) = 1.93$ Å.

However, even this treatment is in all probability incorrect, since the agreement between interatomic distances does not by itself constitute evidence that the anions touch—in any case anions with classical ionic radii. For example, the interatomic distances in binary compounds of the same structural type (NaCl) are [52]§ (Å):

Sm—O	2.49	Np—O	2.50
Pu—O	2.48	Pa—O	2.48
Ce—N	2.50	Gd—N	2.50
Np—N	2.45	Pu—N	2.45

and therefore agree with a precision which is not less than in the previous case. At the same time the O–O or N–N distance in these structures is approximately 3.50 Å, which in no way agrees with the sum of the "classical" ionic radii: $2R(O^{2-}) = 2.80$ Å and $2R(N^{3-}) = 3$ Å. Furthermore, together with such examples, it is not difficult to quote examples of the agreement between distances in structures with different anions and the same cations. For example, the interatomic distances (Å) [52]§ in certain binary compounds of zirconium, tantalum, uranium, and plutonium are

Zr—O	2.31	Zr—N	2.30
Ta—O	2.22	Ta—C	2.22
U—As	2.88	U—Se	2.88
Pu—N	2.45	Pu—C	2.46 ,

If these structures are examined from a purely crystal-chemical standpoint as was done by Lande, it would be logical to assume that the cations are in contact. However, one would then have to adopt for the ionic radii the values $R(Zr) = 1.63$, $R(Ta) = 1.56$, $R(U) = 2.03$, and $R(Pu) = 1.73$ Å, which are completely unacceptable from the standpoint of the "classical" scales (these values lead to the anionic radii $R(O) \simeq R(N) \simeq 0.6$–$0.7$ Å, $R(Se) \simeq 0.85$ Å, etc).

3. "Dimensions" of Ions

The ambiguous nature of any scale of ionic radii leads to the failure also of the second argument in favour of the ionic model. In fact it does not at all follow from experimental data that the "dimensions" of cations are much smaller than the "dimensions" of neutral atoms, while those of anions are much greater. Such a relation is typical only for "classical" scales. On the other hand, in Slater's scale [51,52] ionic radii are almost identical with atomic radii, and in the scale of Levin et al. [53] they differ only slightly from the atomic radii (Table 5). It is noteworthy that the greater anionic radii compared with those

§ Taken from R. W. G. Wyckoff's compilation "Crystal Structures", First Edition, New York, 1948 and checked by the authors against the Second Edition (New York, 1963).

of neutral atoms, required by the classical scale, are not confirmed by calculations of atomic wave functions [54,55]. On the contrary, for halide ions such calculations clearly indicate that the dimensions of the atoms remain unaltered when an electron is attached.

4. Limits of Stability

The Magnus–Goldschmidt limits of stability are usually quoted as the third crystal-chemical argument in favour of the ionic theory. For example, comparison of the O–O distances in the series MgO–CaO–SrO–BaO,

Compound	MgO	CaO	SrO	BaO
O–O distance, Å	2.96	3.40	3.64	3.90

shows that all crystals cannot be represented by close-packed spheres firmly in contact with one another. To explain this fact, it is assumed in classical crystal chemistry that close packing of anions corresponds to the minimum distance between oxygen atoms (in the MgO structure), which is 2.96 Å, and larger distances can be accounted for by the presence of gaps between the anions, which, however, satisfy the familiar "stability limits" [58] for the R(cation)/R(anion) ratio (Table 6).

Table 6. Magnus–Goldschmidt "stability limits" for various structures

Coordination number	Coordination polyhedron	R_A/R_B
2	line	0—0.155
3	triangle	0.155—0.225
4	tetrahedron	0.225—0.414
	square	0.414—0.732
6	octahedron	0.414—0.732
8	cube	0.732—1.000

It is readily seen, however, that these stability limits also cannot be regarded as a confirmation of the validity of the classical ionic radii for at least two reasons. The first is simply that, in fact, the classical ionic radii frequently do not satisfy the Magnus–Goldschmidt rules (Table 7). The second reason consists in the preconception (under the influence of the ionic theory) according to which "large" ions are necessarily assumed to be anions and "small" ions are taken to be the cations [52]. From the purely geometrical standpoint, there is no reason to reject the treatment of structures as close-packed cations (and not anions) [52], for which the stability limits would hold, as it were, "inversely". It is significant, however, that such a view has not merely a geometrical basis. If it is assumed that the negative charge of an atom cannot exceed unity [Sections (IV, 4) and (V, 2)], then we obtain in a natural manner a scale of the radii of singly charged ions of "divalent" elements, already mentioned in Section (III, 1). In this scale the structures of CaO, SrO, BaO, and to a smaller extent MgO consist of close-packed large metallic ions A^+, the octahedral vacancies of which contain the O^- anions, and the stability limits hold in many cases, albeit for the inverse ratio R(anion)/R(cation) (Table 8).

5. Other Methods for the Determination of Ionic Radii

Thus experimental data on interatomic distances do not yield convincing arguments either for or against the ionic theory, so that the classical scales of ionic radii must be regarded not as a basis but as a consequence of the ionic model. This conclusion applies also to other methods for the determination of ionic radii based on attempts to supplement or replace purely crystal-chemical data by other considerations. Such attempts were made at one time by Wasastjerne [42,43] and Pauling [47–49].

Table 7. Examples of the breakdown of the Magnus–Goldschmidt rule

Compound	Structural type	Coord. no., coord. polyhedron	$R(A^{2+})/R(B^{2-})$, (Pauling's radii), Å
BeO	wurtzite	4 tetrahedron	0.22
BeS	zinc blende	»	0.17
BeSe	ditto	»	0.16
BeTe	»	»	0.14
MgSe	NaCl	6 octahedron	0.33
SrO	NaCl	»	0.81
BaO	NaCl	»	0.97
PaO	NaCl	»	0.77
UP	NaCl	»	0.75
NpO	NaCl	»	0.79
PuO	NaCl	»	0.77
AmO	NaCl	»	0.77

Table 8. The ratios $R(B^-)/R(A^+)$ for various crystals

Crystal	Structural type	$R(B^-)/R(A^+)$	Crystal	Structural type	$R(B^-)/R(A^+)$
MgO	NaCl	0.55	FeO	NaCl	0.53
CaO	NaCl	0.45	CaO	NaCl	0.54
SrS	NaCl	0.69	NiO	NaCl	0.56
BaS	NaCl	0.60	CdO	NaCl	0.47
BaSe	NaCl	0.69	PaO	NaCl	0.43
BaTe	NaCl	0.70	UO	NaCl	0.44
TiO	NaCl	0.55	NpO	NaCl	0.43
VO	NaCl	0.58	PuO	NaCl	0.43
MnO	NaCl	0.51	AmO	NaCl	0.43

1. Wasastjerne based his treatment on experimental refractive indices and dielectric constants, assuming that the polarisability of ions α is proportional to their volume V, as for the primitive model of the atom considered as an ideally conducting sphere. Subdivision of the experimental distance (A–B) in the proportions $\sqrt[3]{\alpha_A} : \sqrt[3]{\alpha_B}$ is possible and yields a rough estimate of ionic radii; however, for this purpose it is necessary to divide in some way the overall polarisation of the crystal into increments corresponding to the individual ions. Wasastjerne determined the ionic radii assuming essentially that all polarised electrons belong to anions, but it is readily seen that the other hypothesis would lead to the opposite estimates.

2. Pauling's treatment [47–49], based on the postulate that in crystals the anions of the elements in Groups VII, VI, and V and the cation of the elements in Groups I, II, and III are isoelectronic, suffers from the same defect. Furthermore Pauling was forced to construct this scale of ionic radii in two stages. In the first stage he determined the so called "univalent" ionic radii R_1, assuming that the

corresponding anions are isoelectronic with ions of Group VII elements and that the ionic radius is inversely proportional to the Slater charge of external electrons:

$$R_1 = \frac{C}{Z_{\text{nucleus}} - Z_{\text{screen}}} \quad . \qquad (13)$$

However, the resulting interatomic distances differ appreciably from the experimental values (by about 0.5 Å). Therefore in the second stage Pauling modified the "univalent" ionic radii by introducing a correction for the hypothetical contraction of the ions in the crystal.

It is interesting that Pauling's equation (13) combined with the hypothesis that $A^{II}B^{VI}$ crystals contain only the singly charged ions $(A^{II})^+$ and $(B^{VI})^-$ yields satisfactory values for the interatomic distances also without this modification (Table 9). Then the radii obtained for the ions $(A^{II})^+$ and $(B^{VI})^-$ are found to be fairly close to the values obtained earlier [Section (III, 1), Tables 4 and 5].

Table 9. The ionic radii $R(A^+)$ and $R(B^-)$ and interatomic distances in $A^{II}B^{VI}$ crystals obtained by Pauling's equation (13). The experimental interatomic distances are given in brackets

$R(B^{1-})$	B^{VI}	$R(A^{1+})$			
		1,25	1,55	1,62	1,81
		A^{II}			
		Mg+	Ca+	Sr+	Ba+
0.88	O^{1-}	2.13 (2.10)	2.43 (2.40)	2.50 (2.57)	2.69 (2.76)
1.20	S^-	2.45 (2.60)	2.75 (2.84)	2.84 (2.94)	3.01 (3.18)
1.35	Se^-	2.70 (2.73)	2.90 (2.96)	2.97 (3.12)	3.16 (3.12)
1.55	Te^-	2.80 (2.75)	3.10 (3.17)	3.17 (3.24)	3.36 (3.50)

6. X-Ray Diffraction Data and the Ionic Model

The capacity of the atom to scatter X-rays (atomic scattering factor f_0) is roughly proportional to the number of electrons and therefore should be different for the neutral atom and the ion. Since the sublattices consisting of atoms bearing different charges are displaced relative to one another in the crystal structure, one may hope that the degree of ionisation will influence the details of the diffraction pattern. Attempts to test in this way whether or not the true charge distribution is consistent with the ionic model were frequently undertaken (see, for example, the literature review in Section IV in Urusov's thesis[59]) and one of the most typical of such attempts has been described by Raccah and Arnott[60]. Using three different values[61-63] of the atomic [form (Ed. of Translation)] factor for the doubly charged ion O^{2-} and the atomic [form] factor for the doubly charged ion Mg^{2+}, Raccah and Arnott showed that the divergence factor¶ in these three cases varies in the range 1.721–0.681%. For the two latest values[62,63] of the scattering factors of the O^{2-} ion, the R factor proved to be 0.849 and 0.881%. The results constitute at first sight convincing evidence in favour of the ionic model.

¶ The relative difference between the experimental and theoretical X-ray reflection intensities: $R = (\sum_{hkl} |I_E - I_T|)/(\sum_{hkl} I_E)$.

However, more detailed analysis shows that this conclusion is incorrect. In the first place the calculation of the intensities using the atomic factor for the singly charged ion[64] O^- in the same study led to $R = 1.326\%$, which falls precisely between the values of the R factor for the doubly charged ions (here one should also bear in mind that, while using the scattering factor for the singly charged O^- ion, the authors employed for magnesium the "doubly charged" atomic factor, as before).

Furthermore, there is yet another general consideration which makes any attempt to assess the degree of ionic character on the basis of X-ray diffraction data extremely risky. In any X-ray diffraction study the theoretical atomic scattering f_0 curve is always multiplied by a "temperature correction"

$$f_{\text{temp.}} = e^{-B(\sin\vartheta/\lambda)} \qquad (14)$$

(which has a characteristic value for atoms of each kind) taking into account the thermal vibrations of the atoms in the lattice (see, for example, Porai-Koshits[65]). The temperature corrections for each structure are found separately by an experimental procedure, which is in fact carried out precisely to ensure the minimum discrepancy between the intensities I_E and I_T. Since the atomic scattering factor is also fairly satisfactorily represented by the exponential function

$$f_0(\sin\vartheta/\lambda) \simeq (\text{no. of electrons}) \times e^{-A'(\sin\vartheta/\lambda)^2}, \qquad (15)$$

the resulting atomic temperature factor

$$f = f_0 f_{\text{temp.}} \simeq (\text{no. of electrons}) \times e^{-(A+B)(\sin\vartheta/\lambda)^2} \qquad (16)$$

may simulate the scattering factor for an ion of any charge type†.

IV. EFFECTIVE CHARGES AND THE COVALENT NATURE OF THE CHEMICAL BOND

We see that indirect (thermochemical and crystal-chemical) data cannot be regarded as an argument in favour of the ionic model. However, there also exist at present direct methods for the determination of effective charges of atoms in molecules and crystals. The data obtained with the aid of these methods in fact show that the chemical bond in inorganic crystals is significantly covalent‡.

1. Dipole Moments of Diatomic Molecules

The simplest method for estimating the effective charge lies in the measurement of the dipole moment. In a diatomic molecule A–B the effective charge (expressed as a

† A discrepancy may be observed only in the region of very low values of $\sin\theta/\lambda$ (see the plot in Freeman's paper[66]), particularly for amplitudes which are expressed as the differences between the atomic factors for the ions A and B. Such amplitudes are F_{111} for the NaCl lattice and F_{200} for the ZnS lattice. It is remarkable that an accurate estimate of the intensity of the I_{111} reflection for MgO yields an ionic charge $Z \simeq 1.2$–1.3.[59]

‡ Of course, in the assessment of the reliability of each effective charge obtained by a particular method, one must bear in mind that the concept of the effective charge of the atom in the molecule or crystal is itself to some extent arbitrary and only the values which are reproducible when obtained by different methods may be regarded as reliable [see Section (IV, 5)].

fraction of the electronic charge) can be defined by the relation

$$Z = \mu/4.8R, \qquad (17)$$

where the dipole moment μ is measured in debyes and the interatomic distance R in angstroms. The application of Eqn. (17) to the dipole moments of alkali metal halide molecules (in the gas phase) usually yields charges which are fairly close to $Z \simeq 1$. Recently the dipole moments of the diatomic molecules SrO and BaO were determined by microwave spectroscopy and were extrapolated to BeO (Table 10)[67]. Table 10 shows that the corresponding effective charges do not exceed unity, whereas according to the ionic model charges close to two would be expected in this case.

2. Dielectric Properties of the Crystal Lattice and Ionic Charges

The data in Table 10 do not permit the direct assessment of the effective charges in crystals for which the purely ionic state appears to be energetically the most favourable, since the Madelung constant for crystals is significantly greater than unity while the corresponding value for a diatomic molecule is unity. It is interesting, however, that the charges in Table 10 hardly change on transition to the crystal state. One of the most widely known methods for estimating effective charges in this case is based on the investigation of the dielectric properties of the crystal lattice.

Table 10. The dipole moments μ and effective atomic charges Z for certain molecules

Molecule	μ (D)	Z (e)
BeO	6.3	1.00
SrO	8.9	0.97
BaO	7.9	0.85

Szigetti[68] showed, in terms of the rigid and non-overlapping ion approximation, that the difference between the static (ϵ_0) and high-frequency (ϵ_∞) dielectric constants is related to the effective ionic charge Z by the equation

$$\varepsilon_0 - \varepsilon_\infty = \left(\frac{\varepsilon_\infty + 2}{3}\right)^2 \cdot \frac{4\pi Z^2}{\omega^2 V_m} \qquad (18)$$

where m is the reduced mass of the pair of ions A and B, V the volume per AB formula unit, and ω the frequency of the optical branch of lattice vibrations, which can be found by an independent method.

The effective charges "according to Szigetti"[68-78] are listed in Table 11, which shows fairly clearly the discrepancy with the value based on the concepts of the ionic theory.

The effective ionic charges can also be estimated using elastic and piezoelectric properties of crystals. The estimates obtained in this way, $Z_{BeO} \simeq 1$, $Z_{ZnO} \simeq 1$,[81] $Z_{ZnS} = 0.68$,[82] and $Z_{CdS} = 0.73$[83] or $\simeq 1$ [84] confirm the previous data.

3. Spin–Orbit Splitting

A method for estimating effective charges, which is significantly different from the preceding two, is based on the study of the spin–orbit splitting of levels in the valence band of crystals, which is reflected, for example, in a characteristic subdivision of peaks corresponding to interband transitions[85-87].

Table 11. Effective charges* "according to Szigetti"[68-89]

Crystal	Charge	Crystal	Charge	Crystal	Charge	Crystal	Charge
LiF	0.87[68]	RbI	0.89[68]	PbF_2	0.87[71]	BN	1.14[76]
NaF	0.93[68]	CsCl	0.84[68]	BeO	1.1 [72]	BP	0.25[76]
NaCl	0.74[68]	CsBr	0.79[68]	MgO	1.76[68]	InP	0.60[77]
NaBr	0.69[68]	TlCl	1.08[68]		1.20[79]		
				CaO	1.52[68]	GaAs	0.43[77]
NaI	0.71[68]	CuCl	1.10[68]		1.18[79]		
				SrO	1.16[68]	InAs	0.56[77]
KCl	0.80[68]	CuBr	0.995[68]		1.22[79]		
KBr	0.76[68]	CaF_2	0.74[68]	ZnO	1.06[73]	AlSb	0.48[77]
			0.83[69]	ZnS	0.96[68]	GaSb	0.30[77]
			0.82[70]		0.85[74]		
		SrF_2	0.65[68]				
			0.875[69]				
KI	0.69[68]		0.85[70]	CdS	1.00[74]	InSb	0.34[77,78]
		BaF_2	0.70[68]				
			0.90[69]				
RbCl	0.84[68]		0.86[70]	ZnSe	0.7[75]	Mg_2Si	0.6[80]
		CdF_2	0.79[71]				
RbBr	0.82[68]		0.82[70]	TiO_2	1.48[68]	Mg_2Ge	0.6[80]
						Mg_2Sn	0.6[80]

* For compounds A_2B and AB_2, the effective charge corresponds to the charge at the atom B.

From the standpoint of quantum mechanics, the effective charge of an atom corresponds to the probability p of finding a valence electron at this atom. Spin–orbit splitting is in fact a phenomenon in which the probability of observing the electron at oppositely charged atoms of the crystal is revealed in a fairly direct manner. As a result of the interaction of the spin and orbital momenta, the energy levels of the valence electrons in crystals split[86-88], and each atom makes its own contribution to the overall splitting, proportional to the probability of finding a valence electron at the atom. The resulting splitting Δ can thus be expressed in terms of the splittings for the individual atoms, Δ_A and Δ_B§, in the following form[88]:

$$\Delta \approx p_A \cdot \Delta_A + p_B \cdot \Delta_B, \; p_A + p_B = 1. \qquad (19)$$

All three splittings, Δ, Δ_A, and Δ_B, can be found by an independent method, so that Eqn. (19) makes it possible to determine from experimental data the required probabilities p_A and p_B or, conversely, to compare the experimental splitting Δ_E with the corresponding theoretical value Δ_T calculated with the aid of Eqn. (19) for this or a previously specified effective charge. The corresponding data are presented in Table 12. Comparison of this table

§ We may note that the quantities Δ_A and Δ_B for atoms in a crystal are not necessarily the same as the quantities Δ_A^0 and Δ_B^0 observed in the spectrum of the free atoms. Such agreement occurs at the point L of the valence band (for ZnS type crystals). In the centre of the Γ band $\Delta_A \simeq 3/2\Delta_A^0$ and $\Delta_B \simeq 3/2\Delta_B^0$.

with Table 11 shows that the charges "according to Szigetti", which are of the order of unity for $A^{II}B^{VI}$ compounds and of the order of 0.5 for $A^{III}B^{V}$ compounds, give rise to fully satisfactory agreement between the theoretical and experimental values of spin–orbit splitting.

Table 12. Spin–orbital splitting in crystals*

Crystal	AlAs	GaSb	InAs	InSb	ZnSe	ZnTe	CdSe	CdTe	HgSe	HgTe
Δ_E, eV	0.33	0.75	0.43	0.98	0.35	0.57	0.28	0.55	0.30	0.75
Δ_T, eV	0.33	0.76	0.41	0.89	—	—	—	—	—	—
Δ (B)	—	—	—	—	0.29	0.65	0.29	0.65	0.29	0.65

* For the compounds $A^{III}B^{V}$, the splitting Δ refers to the centre of the zone and for the compounds $A^{II}B^{II}$ to point L. The effective charges used in the calculation of Δ_T for $A^{III}B^{V}$ were taken from Gielisse[76]. The data for the compounds AlAs–InSb were taken from Braunstein and Kane[89] and those for the compounds ZnSe–AgTe from Scouler and Wright[90].

4. X-Ray Spectroscopic Method for the Determination of the Effective Charge

The most direct and convincing evidence against the ionic theory comes, however, from X-ray spectroscopic data for molecules and crystals[91-93]. X-Rays are generated in transitions of outer electrons to inner atomic levels (X-ray emission spectra) and are absorbed in the reverse transitions (absorption spectra). Since the excess charge at the atom (positive or negative) leads to a displacement of the atomic energy levels, the study of the dependence of this displacement on the charge permits the experimental determination of the effective charges of ions in molecules and crystals by comparing their X-ray spectra with those of neutral atoms. The effective charges found by the X-ray spectroscopic method are listed in Table 13, three characteristic features of which are the most important: (1) the "X-ray spectroscopic" effective charges are usually in good agreement with the values estimated by other methods; (2) these charges are close in magnitude to the formal charges of the ionic theory mainly only for compounds of univalent elements; (3) whereas the charges of positive ions may reach fairly high values, those of negative ions do not exceed unity.

The data in Tables 11–13 show that this last property of effective charges is fairly general and is probably particularly important. Its importance is discussed below; here we may note that this feature is confirmed also by more detailed X-ray spectroscopic studies than the investigation of the displacement of the lines in the spectra. In a number of recent studies methods were developed whereby it is possible to assess the general structure of the energy levels and the form of the wave functions of the electrons in molecules and solids. A study of this kind on TiO, for example, showed[97] that the structure of the energy bands of this crystal is best interpreted on the basis of calculations[98] using singly-charged Ti^+ and O^- ions.

5. The Consistency of the Effective Charges and the Concept of the Effective Charge

The data on the effective charges obtained with the aid of the methods discussed above can be objected to on quite natural grounds, associated with the following factors: (1) the inaccuracy of the estimate of the effective charges by each method; (2) the incomplete consistency of different methods with one another; (3) the inadequacy of the concept of the effective charge itself. We shall examine these objections in order to obtain the answer to the question to what extent the effective charges estimated by various "direct" methods correspond to the "true" charges of ions in crystals and consequently to what extent such data really constitute evidence against the ionic theory.

Table 13. Effective charges Z found by the X-ray spectroscopic method*

Crystal	Z	Crystal	Z	Crystal	Z	Crystal	Z
NaF	0.58	MgS	1.05 −1.2	MnS	−0.86 −0.7 [95]	GaSb	0.33 [96]
NaCl	0.92	CaS	−1.1 −0.7 [95]	GeS	−0.71	InSb	0 [96]
NaBr	0.83	BaS	−0.71	SiO_2	1.97	Al_2O_3	1.53 1.77 [96]
NaI	0.75	ZnS	−0.86 −0.66 −0.3 [95]	SiS_2	1.69 −0.81	Al_2S_3	1.26 −1.00
MgF_2	1.30	CdS	−0.81 −1.5 [95]	$FeS_{1,98}$ marcasite	−0.96	Al_2Se_3	1.44
		$FeS_{1,093}$	−0.71 −0.7 [95]	CoS_2	−0.54	Al_2Te_3	1.44
$MgCl_2$	1.50						
$MgBr_2$	1.38	$FeS_{1.018}$	−0.96	NiS_2	−1.1	Mg_2C	0.34
Na_2S	0.75 −0.96	$CoS_{1,09}$	−0.61	MnS_2	−0.15	Li_2Si	−0.09
K_2S	−1.06	NiS	−0.66 −0.7 [95]	SnS_2	−0.54	Mg_2Si	−0.89
Ag_2S	−0.61	CuS	−0.51	AlN	1.32 1.17 [96]	Ca_2Si	−0.89
Cu_2S	−0.61	TiS	−0.61	AlP	0.87 0.87 [96]	Mg_2Sn	0.28
MgO	1.01 0.5 [94]	$TiS_{1.81}$	−0.81	AlSb	0.57 [96]		

* The minus sign denotes throughout the charges of the "electronegative" atom B (obtained from the displacement of the $K_{\alpha_{1,2}}$ doublet for this atom). All the charges, apart from those with individual references, were taken from Refs. 91 and 92.

1. The accuracy of each method may be checked by comparing the charges determined by the same method for different substances, in which the expected charges should have approximately the same value. Comparison of the charges determined, for example, by the method of Szigetti and by X-ray spectroscopic methods for the family of alkali metal halides or alkaline earth metal chalcogenides (Tables 11 and 13) shows that the results usually agree to within about $(0.1-0.3)e$ and therefore each method may be regarded as "accurate" within these limits. For the X-ray spectroscopic method, there exists yet another check, based on the possibility of an independent estimate of the charge at each of the atoms A and B in the binary compound AB. Experiment shows that both charges are usually found to be the same within the accuracy quoted above.

2. The consistency of the effective charges is clearly seen from a comparison of Tables 11–13 and also from Table 14 (taken from Urusov[59]), which lists about ten effective charges in ZnS obtained by a wide variety of methods. These tables show that the effective charges obtained by different methods are as a rule consistent to within the same limits, namely (0.1–0.3)*e*.

Table 14. Comparison of the effective charges in ZnS obtained by different methods

Charge	Method of estimation	References
0.96	Szigetti's method	68
0.85	infrared absorption spectra	74
0.68	measurement of piezoelectric constants	82
0.51	correlation with thermal ionisation of impurities	99
0.8	measurement of hyperfine splitting constant in ESR spectrum of impurity ions	100
0.86	X-Ray spectra	91, 92
0.66		
0.56	measurement of refractions	101
0.5	difference between optical and thermal width of the forbidden gap	102
0.7	study of magnetic susceptibility	103
Mean 0.7±0.2		

3. We shall finally examine the question of the validity of the concept of the effective charge itself, which is important for the understanding of the real significance of various experimental estimates. There is no doubt that the effective charge of an atom in a molecule or crystal is not a physical quantity with a completely valid definition, such as, for example, the mass of the atom or the charge of its nucleus. In fact, effective charges are used for an approximate representation of the real distribution of electron density. In various cases different approximations may be necessary, since, generally speaking, different "effective charges" correspond to different properties. Therefore any experimental method for the estimation of "effective charges" constitutes not only a method of measurement but at the same time also a method for the definition of the concept of the effective charge itself (this explains the discrepancies between the effective charges obtained by different methods). If the effective charges obtained by different methods showed a fairly wide scatter (from zero to the value of the formal valence), then the very concept of a "unique" charge attributable to the atom in the compound would of course lose significance.

However, experiment shows (see paragraph 2) that in fact all these values agree with one another within reasonable limits. Thus reference to the lack of validity of the concept of the effective charge would be justified only if it was possible to exclude altogether this concept from the theoretical scheme of quantum chemistry and the theory of the solid state (and this is scarcely possible at the present time). At any rate, the inaccuracy of this concept cannot serve as a basis for the return to the ionic theory, since the assertion that the charge, say, at the S atom in ZnS is nevertheless −2, already presupposes the use of some definition of the effective charge, for example one of the definitions which have been enumerated. However, experiment shows that *in the same sense* this charge can be much more correctly treated as close to unity.

V. THE PROBLEM OF MULTICHARGED NEGATIVE IONS FROM THE STANDPOINT OF QUANTUM MECHANICS

The small charge of negative ions is a general property of experimental effective charges, as already mentioned above. When Table 13 is examined, it is difficult to avoid the conclusion that it is precisely the impossibility of the attachment to the atom of more than one excess electron that constitutes the physical factor which "regulates" the distribution of charge in molecules and crystals. This conclusion is clearly illustrated in Table 15, which lists the effective charges at the oxygen atom in compounds with a wide variety of compositions and structures.

In this section an attempt is made to show that this conclusion not only follows from experimental data but probably is also a fairly natural consequence of simple theoretical considerations.

Table 15. Effective charges at the oxygen atom[91] in different compounds

Compound	Effective charge	Compound	Effective charge
MgO	1.01	Na_2SiO_3	1.14
SiO_2	0.99	$MgSiO_3$	0.98
Al_2O_3	1.02	$Al_2(SO_4)_3$	0.89
Na_2SO_4	1.09	$Mg(ClO_4)_2$	0.75
Na_3PO_4	1.15	$Al(ClO_4)_3$	0.73
$MgSO_4$	0.88	$Mg_3(PO_4)_2$	0.92
$AlPO_4$	0.94	$KAlSi_3O_8$	1.01

1. Localisation of the Electron and the Bound States

Table 16 lists the experimental values of the first two ionisation potentials and affinities for one electron for a number of "electronegative" atoms. Evidently the electron affinities of all the atoms (except halogens) are smaller approximately by a factor of ten than the ionisation potential, i.e. the binding energy of even one excess electron is always insignificant.

We shall consider this finding from the standpoint of quantum mechanics. The localisation of the electron at the atom (i.e. the presence of a "bound" state in the system electron–atomic residue is possible only when the potential well corresponding to the potential acting on this electron contains a "discrete spectrum" of energy levels¶.

It is known that in any field $U(r) < 0$ which vanishes at infinity, $\lim_{r\to\infty} U(r) = 0$, a discrete spectrum corresponds to negative energies, while a continuous spectrum corresponds to positive energies[104].

Thus Table 16 shows that the dissociation energy of an outer electron depends significantly on the effective charge

¶ The wave functions of a discrete spectrum decay at infinity according to an exponential law, so that the probability of finding an electron outside the atom is very small. On the other hand, the wave functions corresponding to a "continuous spectrum" decay to infinity very slowly. For example, in the case of a coulombic potential they have the asymptotic form[104] $Y_l^m(\theta, \varphi)(1/r)\sin(kr - \pi l/2)$ and decrease as $1/r$. Therefore in the state corresponding to the continuous spectrum the electron can be in no way localised at the atom.

and in the case of negative ions approaches the upper boundary of the discrete spectrum. If it is assumed that the effective charge can have fractional values (as is in fact the case in a molecule or a crystal), then, on the basis of the experimental dissociation energies for $Z = -1, 0, 1, 2, \ldots$, it is possible to plot an $E-Z$ interpolation curve showing the dependence of the energy of the outer electron on the charge at the atom. Curves of this kind for carbon, nitrogen, and oxygen are presented in Fig. 1. Evidently in all cases the $E-Z$ curve crosses from negative energy values to positive values at $Z \simeq -1$, i.e. the electron passes to a state corresponding to a continuous spectrum.

Table 16. Ionisation potentials[27] and electron affinities of various elements

Element	Electron-volts		
	I_2	I_1	F_1
F	34.98	17.42	3.45 [105]
Cl	23.80	13.01	3.61 [105]
Br	19.10	11.84	3.36 [105]
I	19.40	10.45	3.06 [105]
O	35.146	13.614	1.47 [106]
S	23.4	10.357	2.07 [107]
Se	21.5	9.75	1.7 [108]
Te	18.6	9.01	2.2 [108]
N	29.605	14.54	−0.1 [109]
P	19.65	11.0	0.7 [109]
As	20.10	9.87	0.6 [109]

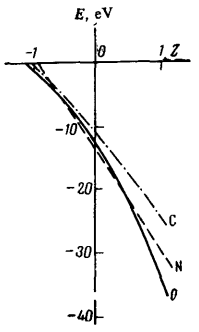

Figure 1.

In this connection one may point to the lack of physical significance of calculations of self-consistent wave functions for ions such as O^{2-}, N^{2-}, etc.[5,110,111] Indeed all such calculations start *a priori* with wave functions having an exponentially decaying radial component of the "Slater" type:

$$R(r) \propto ae^{-ar} \qquad (20)$$

(the parameters of this function are selected by a variational procedure), while functions of this type can be associated only with discrete spectra.

2. Localisation of the Electron in the Case of an Ion in the Lattice

Although Fig. 1 refers to isolated atoms and not to atoms in the lattice, one may assume that the presence of the lattice does not cause any significant change[113]. Fig. 2 presents a schematic curve for the potential U_0 of a given atom B_0 (for example oxygen) and the Madelung potential U_M acting on the electron assuming all the remaining lattice ions to be replaced by point charges. It is evident from Fig. 2 that in the region of B_0 the gradients of both potentials have opposite directions so that the Madelung potential of the lattice weakens rather than enhances the binding of the electron to "its" atom.

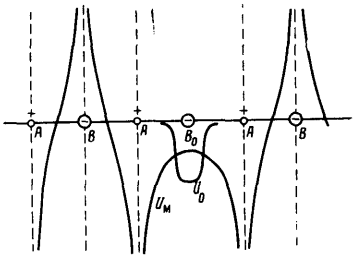

Figure 2.

This consideration can be made more general when account is taken of the fact that in the relevant range of effective charges, $Z_{B_0} \simeq -1$, the U_0 potential becomes of the short-range type and is simulated by a spherical potential well with a rectangular profile[29] (as for the short-range potential of nuclear forces). It is well known that the bound states (states corresponding to a discrete spectrum) in a well of this kind can exist only if the depth of the well u_0 is sufficiently great[104]:

$$u_0 \geqslant \frac{\pi^2\hbar^2}{8ma^2} \qquad (21)$$

(a is the radius of the well).

The experimental fact that the energies of all the outer electrons of all atoms become zero at $Z_{B_0} \simeq -1$ shows that with this effective charge the depth of the well u_0 becomes insufficient to retain the particle. However, it is evident that the Madelung potential U_M (Fig. 2) cannot make the well any deeper, since it reduces the level of its bottom at least to the same extent as it reduces the potential barrier between the atom B and the surrounding atoms A.

It follows from Eqn. (21) that the presence or absence of discrete spectrum levels in the spherical well is determined not only by its depth u_0 but also by its radius a. Therefore one might think that the effect of neighbouring atoms may increase not the depth but the width (radius) of the potential well. Calculation shows, however, that this effect is probably insignificant[112,113].

To make the treatment concrete, suppose that the radius of the well $a = 2$ a.u. $\simeq 1$ Å, i.e. about half the interatomic distance in typical oxides such as MgO. We shall now examine the relation between the depth of the well u_0 and the energy E of the lowest level in this well.

On solving the Schrödinger equation

$$\begin{aligned} &\frac{1}{r}\frac{d^2}{dr^2}(r\psi) + k^2\psi = 0, \quad k = \sqrt{2(u_0 - |E|)}, \quad r \leqslant a \\ &\frac{1}{r}\frac{d^2}{dr^2}(r\psi) - k^2\psi = 0, \quad k = \sqrt{2|E|}, \qquad r > a \end{aligned} \qquad (22)$$

for this potential, it can be shown[104] that the energy of the lowest level is defined as the root of the transcendental equation

$$\sin ka = \pm \sqrt{\frac{1}{2a^2 u_0}} \qquad (23)$$

(the roots with $\cot ka < 0$ must be used[104]). The numerical solution of Eqn. (23) with $a = 2$ a.u. yields the curve relating $|E|$ to u_0 (Fig. 3), which can be more conveniently interpreted as the plot of the opposite function: $u_0 = u_0(|E|)$. We shall now make the reasonable assumption that, for each effective charge Z_B, the outer electron of the atom B is located at the lowest level E in the potential well due to the atomic skeleton and the remaining electrons. Then the dependence on Z of the quantity corresponding to the binding energy $|E|$ may be estimated from the plots in Fig. 1, and, on combining the plots in Figs. 1 and 3, it is easy to find also the relation $u_0 = u_0(Z_B)$. The dependence of the depth u_0 of the potential well on the effective charge of the oxygen atom,

$$u_0(Z) = u_0(|E|), \quad |E| = f(Z) \qquad (24)$$

is shown in Fig. 4. The experimental data allow this curve to be plotted only up to the point $Z = -1$. However, the probable extrapolation of this curve (dashed line) shows that at $Z \simeq -1.2$ the depth of the well u_0 becomes zero. Therefore, even if one assumes that the effect of the lattice can result in a decrease of the radius of the well, with the charge $Z \simeq -1.2$ the volume of the well nevertheless becomes zero and inequality (21) will not hold.

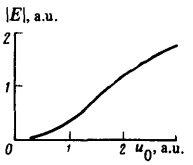

Figure 3.

It must be emphasised yet again that all the arguments adduced above refer only to negative ions. From the standpoint considered, positive ions, both in a free state and in a chemical compound, can have any charge, although excessively large positive charges are unlikely for other reasons. [Section (V, 4)]. Therefore the presence of singly charged ions, say, Ca^+ in CaO, does not contradict chemical facts requiring the presence of the doubly charged ion Ca^{2+}, for example the well known isomorphism of $NaNO_3$ and $CaCO_3$. If it is assumed that the Na atom in $NaNO_3$ indeed exists in the form of the Na^+ ion with a radius of 0.95 Å (which is also not entirely evident), then the similarity of the distances and the isomorphism of both compounds may be attributed to the presence of the doubly charged ions Ca^{2+} and CO_3^{2-} in $CaCO_3$. This leads, however, to an average negative charge at the oxygen atom (about 0.5). This illustrates the obvious fact that polyatomic anions can have charges greater than unity: −2, −3, −4 [for example in $Fe(CN)_6^{4-}$].

3. Other Causes of the Decrease of Ionic Character

The effect involving the "displacement" of the electron to a state corresponding to a continuous spectrum, mentioned above, thus constitutes the principal mechanism restricting the anionic charge to $|Z_{anion}| \simeq 1e$. However, from this point of view, $|Z| \simeq 1e$ must be regarded as only the upper limit of the possible charge. In fact the real charges in compounds can be still lower, due to energy considerations. This conclusion is apparently confirmed by experimental results (see Tables 11–13). In any of the compounds quoted in these tables the charge at the halogen atom may be unity. However, in no case does it actually reach this value. A similar conclusion follows from thermochemical and crystal-chemical arguments. Thus comparison of theoretical and experimental lattice energies of alkaline earth and transition metal halides[32] indicates a considerable departure from the ionic model.

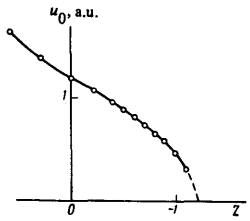

Figure 4.

Such departure from the purely ionic structure, with its characteristic tendency towards close packing, is indicated by much well known crystal-chemical data[58]. Thus, for example, BeF_2 has the open structure of cristobalite, while $BeCl_2$ forms a chain structure. $CaBr_2$ and $CaCl_2$ crystals have a deformed rutile structure with two Ca–Cl distances, namely 2.70 and 2.76 Å. In the $BaCl_2$, $BaBr_2$, BaI_2, $PbCl_2$, and $PbBr_2$ structures each metal atom is generally surrounded by nine halogen atoms at the vertices and at the centre of a trigonal prism, which in the case of $SrBr_2$ is also deformed. Calcium and lead iodides crystalise with the characteristic cadmium iodide layer structure. We may mention, finally, certain facts which suggest that even alkali metal halides are not completely ionic (Tables 11 and 13).

4. Description of the Nature of the Chemical Bond in Partially Covalent Crystals and the LCAO Method

We see that the crystals of inorganic compounds are to a large extent covalent and therefore in conclusion we shall consider the question of the description of the chemical bond in such crystals. The general postulates will be set out using as a typical example alkaline earth metal oxides[53], which makes it possible to demonstrate also how partial covalence can modify the physical properties of a solid.

The very concept of the chemical bond presupposes a definite approach to the theory of the electronic structure

of the molecules or crystals. The principal feature of this approach is that, within the framework of the theory of the chemical bond, we attempt to relate the electronic structure of the entire system to (a) the electronic structure of the constituent atoms of the system and (b) to the interaction of these atoms with one another. In the quantum chemistry of molecules principles (a) and (b) are expressed in the molecular orbital method, where one-electron functions of the entire molecule (molecular orbitals) are derived from the wave functions of the individual atoms (atomic orbitals). From the standpoint of the molecular orbital method, the chemical bond in an individual molecule of the MgO type is described, in the simplest variant, with the aid of a two-centre molecular orbital of the type

$$\psi = c_1\varphi_1 + c_2\varphi_2, \quad c_1^2 + c_2^2 = 1 \qquad (25)$$

$\varphi_1 = 2p_x$ orbital of O atom, $\varphi_2 = 3s$ orbital of Mg atom, where the relative values of the coefficients c_1 and c_2 determine the ionic character of the molecule.

In a coordination crystal of the MgO type individual molecules cannot be isolated. However, this is by no means necessary, since the molecular orbital method is in no way restricted to two-centre two-electron bonds. In this case it is most logical to treat the entire crystal as a giant "molecule" of $N \simeq 10^{24}$ atoms and to use the corresponding one-electron functions as the sum of the atomic orbitals of all the atoms constituting the crystal. This method, which is fully analogous to the LCAO-MO method in molecular theory, is well known in the physics of the solid state under the name "the strong bond method". Although each one-electron function (the so called "Bloch wave function") in the crystal contains a number of atomic orbitals of the order of 10^{24}, the actual application of the strong bond method is greatly simplified by the translational symmetry of the crystal lattice. As a result of the presence of translational symmetry, all the atomic orbitals φ, linked with one another by the translational motion of the lattice R, enter into the one-electron function of the crystal in the form of the combination

$$\psi = \frac{1}{\sqrt{N}} \Sigma_R e^{ikR} \varphi(r - R), \qquad (26)$$

where the summation is carried out over all the lattice sites. If each atom of the crystal has only one atomic orbital (and each unit cell contains only one atom), then Eqn. (26) will be the "true" one-electron function of the crystal (the eigenfunction of the effective one-electron Hamiltonian).

In a more complex case each "kind" of translationally non-equivalent atomic orbital has its own function of the type of Eqn. (26) and the overall one-electron function constitutes a linear combination of similar "basal" Bloch functions. For a crystal of the MgO type such basal Bloch functions are therefore the four functions formed from the $2p_x$, $2p_y$, and $2p_z$ orbitals of the oxygen atom and the ns functions of the metal atoms:

$$\begin{aligned}
\psi_1 &= (1/\sqrt{N}) \Sigma_R \exp(ikR)\, \varphi_1(r - R),\\
\psi_2 &= (1/\sqrt{N}) \Sigma_R \exp(ikR)\, \varphi_2(r - R),\\
\psi_3 &= (1/\sqrt{N}) \Sigma_R \exp(ikR)\, \varphi_3(r - R),\\
\psi_4 &= (1/\sqrt{N}) \Sigma_R \exp(ikR)\, \varphi_4(r - R),\\
\varphi_1 &= 2p_x,\ \varphi_2 = 2p_y,\ \varphi_3 = 2p_z,\ \varphi_4 = ns.
\end{aligned} \qquad (27)$$

Each overall Bloch function for the entire crystal will then constitute a linear combination of these four basal Bloch orbitals with certain coefficients c_1, c_2, c_3, and c_4:

$$\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + e_4\psi_4, \quad |c_1|^2 + |c_2|^2 + |c_3|^2 + |c_4|^2 = 1. \qquad (28)$$

Fully by analogy with the LCAO-MO method for the MgO molecule, the coefficients c_1, c_2, c_3, and c_4 determine the ionic character of the crystal. Thus with $c_4 = 0$, the Bloch function (28) includes only the atomic functions of the anions. This case, like the case with $c_2 = 0$ in Eqn. (25), corresponds to a purely ionic state. With $c_4 \neq 0$, we have different degrees of covalence as a function of the relative value of the coefficient c_4.

We shall now consider briefly how covalence affects the physical (electrical) properties of the crystals, which depend on the structure of its energy levels.

In order to find the energy levels for the diatomic MgO molecules, it is necessary to set up the "secular" equation

$$\begin{vmatrix} \langle\varphi_1|\hat{H}|\varphi_1\rangle - \varepsilon & \langle\varphi_1|\hat{H}|\varphi_2\rangle \\ \langle\varphi_2|\hat{H}|\varphi_1\rangle & \langle\varphi_2|\hat{H}|\varphi_2\rangle - \varepsilon \end{vmatrix} = 0$$

two roots of which, ϵ_1 and ϵ_2, yield the required levels for the ground and first excited states. Quite analogously, in order to find the energy levels for the MgO crystal by the strong bond method, it is necessary to solve the following fourth-order "secular" equation:

$$Det|\langle\psi_i|\hat{H}|\psi_j\rangle - \varepsilon\delta_{ij}| = 0$$

with the basal Bloch functions (27). Since the latter depend on the vector k, each of the roots $\epsilon = \epsilon_i(k)$ also depends on this "wave vector". Ultimately we obtain 4 N different energy levels, which split into four individual "bands" or "zones": $\epsilon_1 = \epsilon_1(k)$, ..., $\epsilon_4 = \epsilon_4(k)$ (certain bands can of course overlap). In the case of the MgO type crystal under consideration the three bands with the smallest energy (partially overlapping) correspond to the 3 N occupied energy levels and form the so called "valence bands" (altogether in an MgO type crystal consisting of N formula units there are 6 N valence electrons, which occupy 3 N levels in pairs). The fourth band with $\epsilon = \epsilon_4(k)$ corresponds to unfilled, excited states. This is the conduction band and is separated from the valence bands by an energy "gap", called the forbidden gap. The width of the forbidden gap E_g is the most important electrophysical characteristic of the crystal and corresponds to the energy of the first optical transition in the molecule.

If the simplest possible approximation is used to calculate the structure of the energy bands, i.e. the treatment is restricted by (a) taking into account only the valence atomic orbitals and (b) taking into account only the interaction between anions and cations, then $E_g \simeq 11$, 9, 10, and 8.5 eV is obtained respectively for the series MgO–CaO–SrO–BaO.[53] These values are almost the same for the entire series, which is clearly inconsistent with experimental data, since in fact the width of the forbidden gap narrows from 8–9 eV[113,114] to about 4 eV[115] on going from MgO to BaO. It can be shown that, by taking into account the interactions between anions and the interaction of the 2s orbital of oxygen with the ns orbitals of the metal atoms, one cannot alter the variation of E_g in the series of oxides[53], so that the observed narrowing of the forbidden gap appears inexplicable at first sight. However, there is another important factor, which has a very pronounced effect on the width of the forbidden gap and which was not taken into account in the above estimate, namely, comparison of the metal–metal distances in oxides and in metals shows that the distances in the oxides are much shorter than in the pure metals. This fact by itself is not, of course, particularly important, since similar shortening is observed also in other compounds, for example in alkali metal halides. In the latter case, however, such decrease of the A^I–A^I distance does not at all suggest actual interaction

between the metal atoms, which are present in the crystal not in the form of neutral atoms but in the form of ions A^+. From the standpoint of the ionic theory, the oxides $A^{II}O$ constitute a fully analogous example. In all $A^{II}O$ crystals the quantity $2R(A^{2+}_{II})$ is smaller than the metal–metal distance and therefore, from the standpoint of the ionic theory, there is no real interaction between the A^{2+}_{II} ions. The situation is different if it is assumed that the $A^{II}O$ crystals contain only singly charged A^{+}_{II} ions. With the aid of the scale of singly charged ionic radii (see Table 5), it is easy to show that the quantity $2R(A^{+}_{II})$ is smaller than the metal–metal distance only for MgO and perhaps CaO. In SrO and particularly BaO real metal–metal interaction is to be expected and it is not difficult to show that even a very low value of the corresponding resonance integral leads to the required sharp narrowing of the forbidden gap[53].

Metal–metal interaction does not occur in purely ionic crystals and therefore it is to be expected that in the isoelectronic series of alkali metal halides NaF–KF–RbF–CsF a significant decrease of E_g should not be observed. Apparently experimental data[116] confirm this conclusion.

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Kurnakov Institute of General and
Inorganic Chemistry, USSR
Academy of Sciences, Moscow

U. D. C. 547.963.3

The Steric Structure of Nucleosides, Nucleotides, and Their Derivatives

N.N.Preobrazhenskaya and Z.A.Shabarova

This review deals with the literature data on the conformations and intramolecular interactions of nucleosides, nucleotides, and their derivatives: nucleotide esters, nucleoside cyclic phosphates, oligonucleotides, nucleoside pyrophosphates (including nucleotide coenzymes), ATP, and nucleotidopeptides.
The problem of the degree of bending of the pentofuranose ring and its effect on the orientation of the ring substituents, including the effect on the structure of the *cis*-2',3'-glycol group, which is revealed in a number of specific reactions, is discussed together with the question of the relative positions of the base and sugar in nucleosides. The bibliography includes 268 references.

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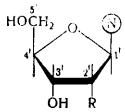
I. INTRODUCTION

During the last decade an enormous amount of data on the properties and structure of nucleosides, nucleotides, and their derivatives has accumulated. It has been established unambiguously that nucleotides are as a rule *N*-glycosides of D-ribose or 2-deoxy-D-ribose†. In all nucleosides the carbohydrate residue is in the cyclic furanose form. The glycosidic centre in the nucleosides has the β-configuration (*trans*-position of C_1,-N and $C_{2'}$-$O_{2'}$ bonds or *cis*-position of $C_{1'}$-N and $C_{4'}$-$C_{5'}$)‡.



R = OH or H, (N) - purine or pyrimidine base

The studies on the determination of the configuration of nucleosides carried out with the aid of refined chemical methods by Todd's school are recognised as classical and are described in a number of reviews including reviews in the Russian language[1-3]. In recent years much attention has been devoted to physicochemical methods for the determination of the configuration of nucleosides, among which NMR spectroscopy[4-8] and spectropolarimetry[9-20] are undoubtedly promising.

At the present time the chemistry of nucleosides has reached a level such that it is necessary to investigate not only the configurations (i.e. the distribution of atoms about the dissymmetric part of the molecule—for example the asymmetric carbon atom or ring), but also the real geometrical formula of the molecules as a whole—their conformation. This problem is particularly important in connection with the study of various polyfunctional derivatives of nucleosides, in which the specific steric structure of the molecule can lead to the interaction and hence the modification of the properties of groups which are not directly linked.

†In this review we shall not deal with synthetic and natural anomalous nucleosides (the "minor" components of nucleic acids and nucleoside antibiotics), among which may be derivatives of sugars other than D-ribose and 2-deoxy-D-ribose and also *C*-glycosides.

‡The following abbreviations have been adopted in the present review: RNA and DNA—ribonucleic and deoxyribonucleic acid respectively; UMP—uridine 5'-monophosphate; ADP—adenosine 5'-diphosphate; ATP—adenosine 5'-triphosphate; NDPS—nucleoside diphosphate sugar; UDPG—uridine diphosphate glucose; NAD—oxidised nicotinamide-adenine dinucleotide; NADP—oxidised nicotinamide-adenine dinucleotide phosphate; NADH—reduced nicotinamide-adenine dinucleotide; FAD—flavine-adenine dinucleotide; THF—tetra hydrofuran; NMR—nuclear (here as a rule proton) magnetic resonance; ESR—electron resonance.

2. RIBOSE AND 2-DEOXYRIBOSE

The form of the nucleoside molecule is to a large extent determined by the conformation of the five-membered carbohydrate ring. The tetrahydrofuran ring, which constitutes the basis of ribose and 2-deoxyribose, is nonplanar like cyclopentane[21], since all its C–C bonds would then have the eclipsed conformation characterised by maximum energy[22]. Due to the effect of the oxygen atom in the furanose ring, more and less stable conformations appear when the ring is bent. It is readily seen that, when the C_2 or C_3 atom deviates from the plane of the ring, a greater number of bonds passes from the eclipsed to the *gauche*-conformation than when the C_1, C_4, or the oxygen atom deviates from the plane of the ring. Accordingly the

conformations with the C_2 or C_3 (or both) atoms outside the ring are more stable.

The deformation of the ring of D-ribose and its 2-deoxy-derivative probably occurs even more readily than in tetrahydrofuran, since the *gauche*-disposition of the OH groups and the CH_2OH group leads to an even greater energy gain, compared with the eclipsed disposition, than the *gauche*-disposition of the hydrogen atoms in tetrahydrofuran. Furthermore, it has been found that the average length of the C_2–C_3 bond in many ribose derivatives is 1.528 ± 0.008 Å[23] (i.e. is close to the value 1.533 ± 0.003 Å found for the ordinary C–C bond[24]). In this case with the eclipsed disposition of the 2- and 3-hydroxyls the distance between their oxygen atoms must be less than 2.5 Å. Since the van der Waals radius of oxygen is 1.40 Å,[25] evidently a planar conformation of the ribose ring is impossible[26].

By analogy with tetrahydrofuran, the most favourable conformations for ribose are those in which the C_2 or C_3 atoms deviate from the average plane of the ring[27,28]. This is the so called primary or main deformation of the furanose ring. The out-of-plane atom (C_2 or C_3) can be displaced to the side where the C_5 atom is located or to the opposite side. This corresponds to possible *endo*- and *exo*-conformations. The deviation of the out-of-plane carbon atom from the average plane of the ring is very considerable: 0.5–0.6 Å. It is interesting that the *endo*-conformation is most often encountered in nucleosides (see Table 1).

Here, however, one should note that the eclipsed or partially eclipsed conformation of the C_2,–C_3, bond in 2-deoxyribose is characterised by a lower strain compared with ribose and can probably actually occur in solution (because there is a hydrogen atom in the 2-position and not an OH group as in ribose). Indeed a conformation of the carbohydrate ring in which the ring oxygen atom is displaced from the average plane of the ring, and not the C_2, or C_3, atom, has been in fact observed with the aid of NMR spectroscopy for a number of deoxyribose nucleosides (thymidine, deoxyuridine, deoxyadenosine 3′-phosphate) (*O-endo*-conformation, see Table 1)[29,30].

Table 1. Conformation of the pentose ring in nucleosides and nucleotides.

Compound	X Ray diffraction data		NMR spectroscopic data	
	conformation	references	conformation	references
Ribose-5-phosphate	C_2,-*endo*	31		
Uridine	C_3,-*endo*	28		
Cytidine	C_3,-*endo*	28. 32. 33	C_3,-*endo*	48
5-Bromouridine	C_2,-*endo*	34		
Adenosine	C_3,-*endo*	28		
Adenosine-5-bromouridine complex	C_3,-*endo* C_3,-*endo*	35		
Uridine 5′-phosphate	C_2,-*endo*	36		
Uridine 3′,5′-cyclic phosphate	C_3,-*endo*	37		
Cytidine 3′-phosphate	C_2,-*endo*	38—41	C_3,-*endo*	48
Adenosine 5′-phosphate	C_3,-*endo*	42—44	C_2,-*endo*	48
Adenosine 3′-phosphate	C_3,-*endo*	45		
Adenosine 3′,5′-cyclic phosphate	C_4,-*exo*	46		
Adenylyl-(2′–5′)-uridine Adenosine residue Uridine residue	C_2,-*endo* C_3,-*endo*	47		
Thymidine	C_3,-*exo*	49 *	O-*endo*	29. 30
Deoxyuridine			O-*endo*	29. 30
5-Fluorodeoxyuridine	C_2,-*endo*	38		
5-Bromodeoxyuridine	C_2,-*endo*	34. 51		
5-Iododeoxyuridine	C_2,-*endo*	52		
Deoxyadenosine	C_3,-*exo*	53		
Deoxyguanosine-5-bromodeoxy-uridine complex	C_2,-*endo* C_2,-*endo*	54		
Thymidine 5′-phosphate	C_3,-*endo*	55		
Deoxyadenosine 5′-phosphate			O-*endo*	29. 30

*Thymidine is the only nucleoside whose structure was also investigated by ESR spectroscopy[50].

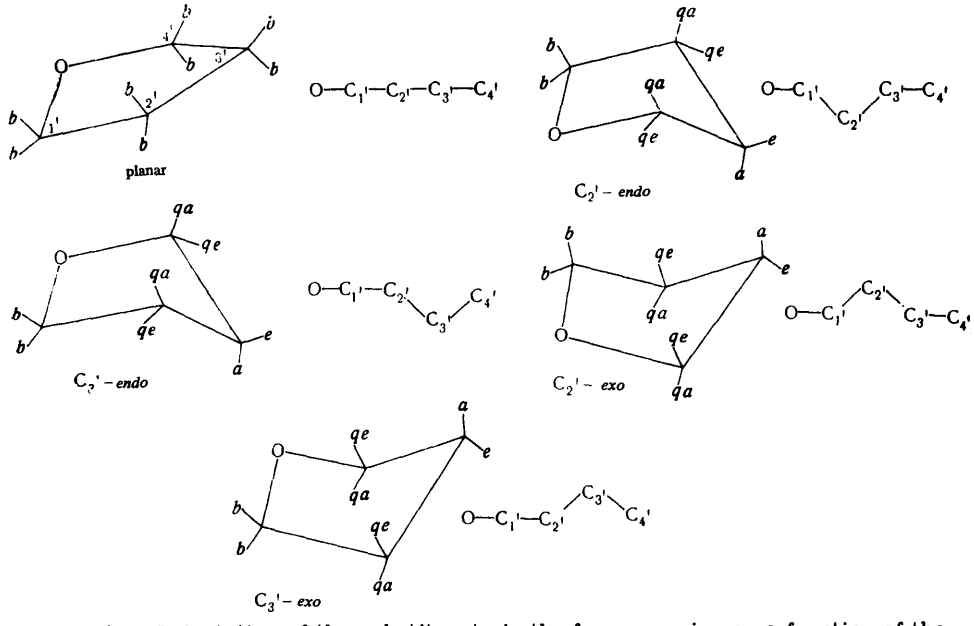


Figure 1. Orientation of the substituents in the furanose ring as a function of the nature of its bending (*a* and *e*—axial and equatorial respectively, *qa* and *qe*—quasi-axial and quasiequatorial, *b*—bisector orientation).

Apart from the primary (main) bending, secondary (minor) bending occurs in the ribose residue of nucleosides: as a rule, the four atoms of the ribose ring, determining its average plane, are also not completely coplanar. However, in this case the deviation is outside the limits of the experimental error, not exceeding 0.05 Å (i.e.8–10% of the primary bending)[38].

The consequences of the bending of the furanose ring in nucleoside are deviations of the C–C and C–O bond lengths from the normal values (up to ±0.11 Å) and of the valence angles from the tetrahedral value (up to ±9°)[21,28-53].

The external angles and bond lengths in the ribose ring also deviate from the normal values. As a result, the substituents at the carbon atoms of ribose are oriented as shown in Fig. 1. Here, however, one should note that, according to NMR spectroscopic data, the orientation of substituents depends to some extent on their nature: in the isomeric 2′- and 3′-*O*-benzylnucleosides the angle of twist between the $C_1,-H_1$, and $C_2,-H_2$, bonds is smaller in the 2′ isomer than in the 3′-isomer[56].

3. CONFORMATION OF THE HETEROCYCLIC BASE

X-Ray diffraction analysis of nucleosides and nucleotides showed that the heterocyclic bases are in many cases almost planar, i.e. the deviations of the ring atoms from the average plane are within the limits of experimental error[32,35,36,45,47,55] (see also Nyburg's review[57]).

However, a number of cases have been described in which the atoms of the base were found to deviate from coplanarity. The bending is particularly pronounced in pyrimidine derivatives. For example, in cytidine[38] and cytidine 3′-phosphate[21,30] the N_1 and C_4 atoms deviate from the average plane of the base to the same side§. The deviations amount to about 0.05 Å, so that the pyrimidine base adopts the form of a shallow boat. In purines the deviations of the heterocyclic ring atoms from the average plane are somewhat smaller.

At the same time the substituents in the heterocyclic rings of nucleotides and nucleosides (the amino-group, oxygen, the methyl group, the C_1, atom of pentofuranose) are displaced from the average plane of the ring very considerably. The O_2 and C_1, atoms (and also the O_4 and C_7 atoms in thymine) deviate to opposite sides[32,36,52]. The displacement of the C_1, carbon atom of ribose from the average plane of the heterocycl probably constitutes a general rule and reaches a considerable magnitude (up to 0.2–0.3 Å).[18,22,34,36,41,47] As a result the glycoside bond forms an angle with the plane of the base[34], which is 3.5° in adenosine 3′-phosphate for example.

4. RELATIVE POSITIONS OF THE BASE AND SUGAR

The relative positions of the base and sugar play an important role in determining the geometrical form of the nucleoside molecule. A clear albeit an incomplete idea of this is provided by the value of the dihedral angle between the average planes of the base and sugar. It is interesting to note that as early as 1947 Astbury believed, on the basis of the X-ray diffraction data obtained by Hendricks[58], that the planes of the heterocyclic base and the carbohydrate in nucleosides are parallel (quoted after Jordan[59]). However, in 1950 Furberg[28] showed that this conclusion is a result of an incorrect interpretation of the experimental data and that in fact the rings in nucleosides are approximately perpendicular to one another. This proved to be true of all the nucleosides and nucleotides investigated hitherto (see Table 2).

Table 2. Dihedral angles between the planes of the base and the sugar in nucleosides and nucleotides.

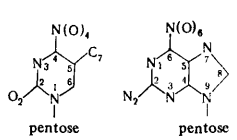
Compound	Angle, °	Refs.
Cytidine	76	21
Thymidine	89	49
	90	50
Deoxyadenosine	69	53
Adenosine-5-bromouridine complex	70 69	35
5-Iododeoxyuridine	81	51
Deoxyguanosine-5-bromodeoxycytidine complex	69 77	54
Adenosine 5′-phosphate	76	43
Adenosine 3′-phosphate	55	45
Thymidine 5′-phosphate	75	55
Uridine 3′,5′-cyclic phosphate	60, 62 *	37
Adenosine 3′,5′-cyclic phosphate	138, 137 *	46

*The dihedral angles for the two conformations existing in a single crystal cell (for further details, see Russ. p. 232).

Evidently, for the same dihedral angle between the planes of the base and sugar, there is a possibility of rotation of the base about the glycosidic bond. Therefore, in order to characterise completely the relative positions of the base and sugar, it is necessary to know the magnitude of the angle of twist φ_{CN}. This is the angle formed by the projections of the bonds $C_1,-O_1$, and N_1-C_6 (for pyrimidines) or N_9-C_8 (for purines). If the N_1-C_6 bond of pyrimidine (or the N_9-C_8 bond of purine) and the $C_1,-O_1$, bond of the sugar are antiparallel, then φ_{CN} is believed to be 0°; positive angles are reckoned clockwise and negative angles anticlockwise looking in the direction from C_1, to N.[39,40]

There exist two regions of φ_{CN} angles in which relatively stable conformations may exist: the region with φ_{CN} about −30° (the *anti*-region) and the region with φ_{CN} about +150° (the *syn*-region). Each of these occupies somewhat more than 90°. Examination of molecular models[60] and also calculations based on the results of X-ray diffraction analysis[61] showed that the barrier between the *syn*- and *anti*-regions is determined by steric interactions between the N_3 atom of the base and the oxygen atom of the pentose ring in purine nucleoside and between the oxygen atom of the 2-oxo-group or the hydrogen at the C_6 atom of the base on the one hand and the oxygen atom of the pentose ring or the oxygen at the C_2, atom of the sugar (the hydrogen at the C_2, atom in deoxyribonucleosides) on the other in pyrimidine nucleosides. For most of the

§In this review the system of numbering of the pyrimidine and purine rings adopted in Chemical Abstracts is employed:



nucleosides and nucleotides investigated, the *anti*-orientation of the base is preferred (see Table 3). The *syn*-orientation is as a rule less favourable sterically. Furthermore, for purine nucleoside in which the C_3, atom deviates from the plane of the sugar and for pyrimidine nucleosides with the C_3,-*endo*-conformation of the sugar, the existence of the *syn*-isomers is altogether impossible[61]. However, it is evident that in pyrimidine O_2-5′-cyclonucleosides and in purine N_3,-5′-cyclonucleosides only the *syn*-orientation of the base is possible in consequence of the formation of an additional ring. This was confirmed by X-ray diffraction analysis[62] (see Fig. 2). Nor can one exclude the possibility that the necessary stabilisation of the *syn*-conformation is achieved in certain cases in the polynucleotide chain[61] or in nucleotidopeptides (see Section 12) due to non-covalent interactions.

Table 3. Orientation of the base and sugar in nucleosides and nucleotides.

Compound	φ_{CN}, °	Refs.
Cytidine	−18	32
5-Bromouridine	−56	34
Thymidine	−39	49
5-Bromodeoxyuridine	−43	34
5-Iododeoxyuridine	−67	52
Deoxyadenosine	− 3	51
Adenosine-5-bromouridine complex	−10 −20	35
Deoxyguanosine-5-bromodeoxycytidine complex	+138 −61	54
Uridine 5′-phosphate	−43	36
Uridine 3′,5′-cyclic phosphate	−72,−56 *	37
Thymidine 5′-phosphate	−48	55
Cytidine 3′-phosphate	−42.1	39
Adenosine 5′-phosphate	−18	43
Adenosine 3′,5′-cyclic phosphate	−5.0,+102 *	46
Adenylyl-(2′–5′)-uridine Adenosine residue Uridine residue	−55 −5	47

*See the footnote to Table 2.

There is a hypothesis that the *anti*-orientation of the base in ribonucleosides may be stabilised by the formation of a hydrogen bond between the 2′-hydroxy-group of ribose and the 2-oxo-group of pyrimidine or the N_3 atom of purine. This hypothesis is supported by a number of factors: (1) the ultraviolet absorption spectra of pyrimidine ribonucleosides change appreciably in a highly alkaline medium; such changes were not observed for the corresponding nucleoside 2′-phosphates[63–68]; (2) the basicity of the heterocycle in ribonucleosides is lower than in the corresponding 2′-deoxyribonucleosides[63,64,68–70]; (3) in the infrared spectrum of 3′,5′-di-*O*-acetyladenosine there is an absorption band corresponding to an intramolecular hydrogen bond; a band of this kind is absent from the spectrum of 2′,5′-di-*O*-acetyladenosine[71]; (4) the 2′-hydroxy-group of the ribose residue in nucleosides is more acid than the 3′-hydroxy-group[67,72–75]—this has a significant influence on a number of reactions: in the methylation of ribonucleosides with diazomethane 2′-*O*-methylnucleosides are formed preferentially[76–79] and in the tritylation of uridine[80–83] and tosylation of 5′-*O*-trityluridine[84] the 2′-hydroxy group is attacked appreciably faster than the 3′-hydroxy group; (5) the study of the rate of hydrolysis of a number of ribodinucleotides also led Witzel to the hypothesis of the existence of the hydrogen bond C_2,–O–H...O=C_2 in pyrimidine nucleosides and C_2,–O–H...N_3 in purine nucleosides[85,86]; (6) in the latest papers from Ts'o's laboratory[87] the results of an NMR spectroscopic comparison of adenosine with 2′-deoxyadenosine and 2′-*O*-methyladenosine and of pyrimidine ribonucleoside 5′-phosphates with 2-deoxyribonucleoside 5′-phosphates are regarded as evidence of the existence of a hydrogen bond between the 2′-hydroxy-group of the sugar and the 2-oxo-group of pyrimidine or the N_3 atom of purine.

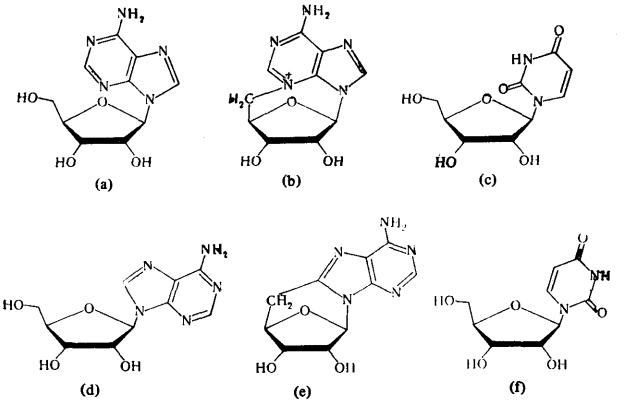
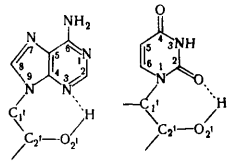


Figure 2. *Syn*- (a, b, and c) and *anti*- (d, e, and f) orientation of the base.

The latter type of hydrogen bond was postulated by Zamecnik[88] in the discussion of the mechanism of the formation of aminoacyl-*t*-RNA from aminoacyladenylates[88].



However, there are a number of data inconsistent with the hypothesis of the existence of such an intramolecular hydrogen bond. Thus in the study of the photochemical addition of water to the 5,6-double bond in pyrimidine nucleosides comparison of the quantum yields for cytidine, 2′-deoxycytidine and cytidine 2′-,3′-, and 5′-phosphates led to the hypothesis that a hydrogen bond forms between the base and the 5′-hydroxy-group of ribose[89,90]. Pitha et al.[91], who observed in the infrared spectra of 2′,3′-di-*O*-substituted nucleosides absorption bands corresponding to a hydroxy-group involved in the formation of a hydrogen bond with the heterocycle, arrived at the same conclusion. Izatt et al. observed a sharp decrease of the acidity of the secondary hydroxyl both in 2′- and in 3′-deoxy-(and methyl-)adenosine and on this basis suggested that a hydrogen bond between 2′- and 3′-hydroxy-groups exists in adenosine[74,75]. It should be noted, however, that this hypothesis does not explain precisely why the 2′-hydroxy-group is the more acid. Finally, on the basis of the determination of the dissociation constants of the 5′-hydroxy-group in the α- and β-isomers of pseudouridine (5-ribofuranosyluracil), Ofengand and Schaefer[92] concluded that the C_5,–O–H...O=C_4 hydrogen bond forms in the natural β-isomer.

5. CONFORMATION OF THE *cis*-GLYCOL GROUP C_2,(OH)–C_3,(OH)

The *cis*-glycol group C_2,(OH)–C_3,(OH) determines a number of important properties of ribonucleosides. Its steric structure can be characterised by the magnitude of the angle of twist φ_{00} between the C_2,–O_2, and C_3,–O_3, bonds. The angle of twist between the true *cis*-bonds is 0°. However, in nucleosides, at least in the solid state, the 2'- and 3'-hydroxy groups deviate from the true *cis*-conformation, which is a consequence (or the cause) of the bending of the ribose ring (see above), and the angle of twist φ_{00} is 43–54°.[23,45] Nevertheless the angle of twist φ_{00} is appreciably less for ribose and other sugar derivatives with the *cis*-glycol group than for sugars with the *trans*-disposition of the 2- and 3-hydroxy-groups, for which the minimum value of φ_{00} is 75° [38] (but not 180° as for the true *trans*-configuration). Thus, as a result of the deformation of the pentose ring, the difference between the values of φ_{00} for the *cis*- and *trans*-isomers is not as great as might have been expected, but it is sufficient to account for the fundamental differences in the reactivities of the compounds. It is known, that in contrast to *trans*-2,3-sugars, ribose derivatives readily react with formation of 2,3-cyclic compounds. A wide variety of 2',3'-alkylidene (isopropylidene, benzylidene, *p*-anisylidene, etc.) derivatives of nucleosides (see, for example, Refs. 1, 2, and 93–101), 2',3'-orthoformates[102] and orthocarbonates[103], 2,3'-carbonates and thiocarbonates[103–112], 2',3'-phenylboronates[113,114], 2',3'-cyclic phosphates (see, for example, Refs. 1, 2, and 114–119), and 2',3'-cyclic phosphites of nucleosides[120] and also of 2',3'-epoxynucleosides[1,121,122] have been described¶. The high rate of oxidation of ribonucleosides with lead tetra-acetate, osmium tetroxide, and periodate, is associated with the ease of formation of intermediate 2',3'-cyclic derivatives[38,123].

The lability of nucleoside 3'-phosphate esters in an alkaline medium is explained by the presence of an adjacent *cis*-hydroxy-group (see, for example, Refs. 1, 2, 93, and 124–126). The elucidation of this effect of the 2'-hydroxy-group assisted in the determination of the structure of RNA (see, for example, Refs. 1, 2, 93, 127 and 128).

There is a hypothesis that the presence of the *cis*-hydroxyl contributes to enhanced activity of the ester group in the *O*-aminoacyl derivatives of adenosine and *t*-RNA in consequence of the formation of a hydrogen bond between the 2'-hydroxy-group and the carbonyl oxygen of the aminoacyl residue[87–128]. In the majority of ribonucleosides and nucleotides in the crystalline state, the C_2,–O_2, and C_3,–O_3, bonds were found to have the *tg*-conformation, i.e. the O–H bond (O–P bond in 3'-phosphate) is oriented *trans* relative to the C_2,–C_3, bond and its orientation is *gauche* relative to the C_2,–C_1, bond or correspondingly the C_3,–C_4, bond (see Fig. 3).

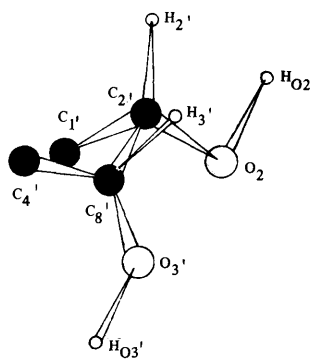


Figure 3. Conformation of the *cis*-glycol group (C_2,-*endo*-bending of the ribose ring).

6. CONFORMATION OF THE C_4,–C_5, BOND

For the exocyclic carbon–carbon C_4,–C_5, bond in the crystalline state, three types of conformation were observed (see Table 4 and Fig. 4): (a) *gg*—*gauche*-orientation of the C_5,–O_5, bond relative to the C_4,–O_1, bond and relative to the C_4,–C_3, bond; (b) *gt*—*gauche*-orientation of the C_5,–O_5, bond relative to the C_4,–O_1, bond and *trans*-orientation relative to the C_4,–C_3, bond; (c) *tg*—*trans*-orientation of the C_5,–O_5, bond relative to the C_4,–O_1, bond and *gauche*-orientation relative to the C_4,–C_3, bond.

Table 4. Conformation of the C_4,–C_5, bond in nucleosides and nucleotides

Compound	conformation	$\varphi_{OO'}$, °	$\varphi_{OC'}$, °	Refs.
Ribose-5-phosphate	*gg*	67	56	31
Cytidine	*gg*			28, 32
Thymidine	*gt*			49
5-Fluorodeoxyuridine	*tg*	173	68	52
Deoxyadenosine	*gt*	68	173	23
Uridine 5'-phosphate	*gg*	54	70	36
Uridine 3',5'-cyclic phosphate	*tg*	176,174*	63,60*	37
Cytidine 3'-phosphate	*gg*	75	44	39,40
Thymidine 5'-phosphate	*gg*	60	57	55
Adenosine 5'-phosphate	*gg*	78	40	42, 43
Adenosine 3'-phosphate	*gt*	56.7	171.7	45
Adenylyl-(2'–5')-uridine				
Adenosine residue	*gg*	73	45	47
Uridine residue	*gg*	62	57	

*See the footnote to Table 2.

As shown in Table 4, the *gg*-conformation is encountered most frequently, at least in the crystalline state. Probably this is because in this conformation the intramolecular interaction between the substituent at the C_5, atom, the base, and the sugar ring is a minimum[21].

7. STRUCTURE OF THE PHOSPHATE RESIDUE IN NUCLEOTIDES

It has been found for the crystals of all the nucleotides investigated that, when the 5'-hydroxy group is esterified by a phosphate residue (nucleoside 5'-phosphate), the O_5,–P bond occupies the *trans*-position relative to the C_4,–C_5, bond, thus ensuring the most extended form of the molecule.

¶Owing to the large number of studies in the field of 2',3'-cyclic derivatives of ribonucleosides, it is not claimed that the selection of literature on this problem presented here is exhaustive.

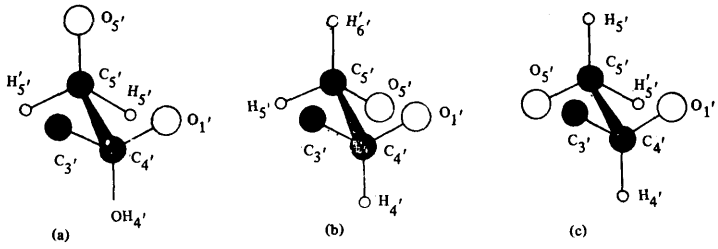


Figure 4. Conformation of the C_4,–C_5, bond: a) *gg*; b) *gt*; c) *tg*.

The phosphate residue in nucleotides in the crystalline form and in neutral solutions is present at the monoanion (this applies to both 3'- and 5'-phosphates). The P–O distance in nucleotides, as in other phosphoric acid esters[129–131], proved to be much shorter (by 0.24–0.09 Å[23, 36,38,43–45]) than the calculated value of 1.71 Å,[132] the bond length decreasing in the following sequence: P–OR > P–OH > P–O' > P=O. This confirms the presence in phosphoric acid esters of π-conjugation between the *d*-orbitals of phosphorus and the *p*-electrons of oxygen[133,134]. In other words, the phosphorus–oxygen bond in phosphoric acid esters has partial double bond character[133]. The decrease of the double bond character between the phosphorus and oxygen as a result of the breakdown of p_π–d_π conjugation results in a significant weakening of the phosphate ester bond. This happens, for example, in nucleoside cyclic phosphates.

8. NUCLEOSIDE CYCLIC PHOSPHATES

Nucleotides can form both five-membered 2',3'-cyclic phosphates and six-membered 3',5'-cyclic phosphates. The five-membered phosphate rings are strained[1,135], which is the main reason for their extremely great reactivity compared with non-cyclic-esters[1,93,135,136].

Probably in consequence of the strain of the five-membered phosphate ring, p_π–d_π conjugation between the oxygen and phosphorus breaks down, which is the reason for the lability of the P–O bond[134]. The much greater stability of the six-membered nucleoside 3',5'-cyclic phosphates is evidence of a lower strain of the ring. However, it follows from a comparison of the time required for 50% decomposition in 1 *N* sodium hydroxide at 100°C of thymidine 3',5'-cyclic phosphate, in which the six-membered phosphate ring is formed with participation of the *trans*-hydroxy-groups[137], 1,2-isopropylidenexylofuranose-3,5-cyclic phosphate, in which a phosphate ring of the same size is formed by *cis*-hydroxy-groups[136,138], and propane-1,3-diol cyclophosphate[136] (2,4, and 72 h respectively) that in nucleoside 3',5'-cyclic phosphates the phosphate ring is also strained, probably as a result of the *trans*-orientation of the C_4,–C_5, and C_3,–O_3, bonds relative to the pentose ring. Because of this configuration of the sugar, the only possible form of the six-membered phosphate ring is the chair conformation. For it to exist, the nature of the bending of the furanose ring must be altered and the C_3,-*endo*-C_4,-*exo*-conformation is the most probable[48,139]. Indeed, studies with the aid of X-ray diffraction showed that in the conversion of uridine 5'-phosphate into uridine 3',5'-cyclic phosphate the conformation of ribose changes from C_2,-*endo*-[36] to C_3,-*endo*-[37] and in the conversion of adenosine 5'-phosphate into adenosine 3',5'-cyclic phosphate the change is from C_3,-*endo*-[42,44] to C_4,-*exo*-[46] (Table 1). The change of the conformation of pentose probably entails the occurrence of some strain in the furanose ring. This is believed[136] to be the cause of the lowered stability of the glycoside bond in nucleoside 3',5'-cyclic phosphates compared with the corresponding nucleosides and nucleotides. On treatment with 1 *N* sodium hydroxide at 100°C, adenosine 3',5'-cyclic phosphate yields adenine, while under these conditions adenosine itself is stable[140]; thymidine 3',5'-cyclic phosphate splits off thymine completely on treatment with 0.1 *N* hydrochloric acid at 100°C for 5 min, while thymidine 5'-phosphate remains stable for more than 3 h under these conditions[136].

An interesting feature of the structure of nucleoside 3',5'-cyclic phosphates is the presence in the same crystal cell of two molecules with different conformations of the glycoside bond; in uridine 3',5'-cyclic phosphate both molecules have the *anti*-orientation of the base relative to the sugar[37], but in adenosine 3',5'-cyclic phosphate one molecule has the *anti*-orientation and the other the *syn*-orientation[46] (so far this is only the second, after deoxyguanosine, case of *syn*-orientation, see Table 3).

9. INTRAMOLECULAR INTERACTIONS IN NUCLEOTIDE ESTERS

When nucleotide esters other than cyclic phosphates are examined, the dependence of the properties of the phosphodiester group on the nature of the substituents in the sugar ring is striking. Thus it is known that *p*-nitrophenyl esters of various nucleotides are hydrolysed in different ways: *p*-nitrophenyl esters of thymidine 3'- and 5'-phosphates are hydrolysed with alkali via the intermediate formation of thymidine 3',5'-cyclic phosphate[141,142], while this behaviour was not observed for the *p*-nitrophenyl ester of uridine 5'-phosphate[142]. The different mechanisms of hydrolysis may be associated with the different conformations of the pentose ring, which may favour or hinder the mutual approach of the 3'-hydroxy-group and the 5'-phosphate group. In uridine 5'-phosphate and thymidine 5'-phosphate crystals different conformations of the carbohydrate ring have indeed been observed (see Table 1). Unfortunately the data are so far insufficient to confirm or reject this hypothesis.

The interaction of hydroxy- and phosphate-groups in *trans*-positions occurs also in other nucleotide derivatives. For example the formation of adenosine 3',5'-cyclic phosphate in the hydrolysis of ATP with barium hydroxide[140],

and the conversion of the methyl ester of thymidylyl-(3′–*N*)-phenylalanine into thymidine 3′,5′-cyclic phosphate on standing in dimethylformamide[143] have been described (for a more detailed treatment, see Section 12).

10. DINUCLEOSIDE PHOSPHATES AND OLIGONUCLEOTIDES

Dinucleoside phosphates constitute a special group of nucleotide esters. The study of adenylyl-(2′–5′)-uridine by X-ray diffraction revealed almost parallel disposition of the two bases and their partial overlapping[39] (Fig. 5). The study of solutions of dinucleoside phosphates and di-, tri- and oligo-nucleotides shows that the parallel orientation of the bases is most likely for these compounds also in solution.

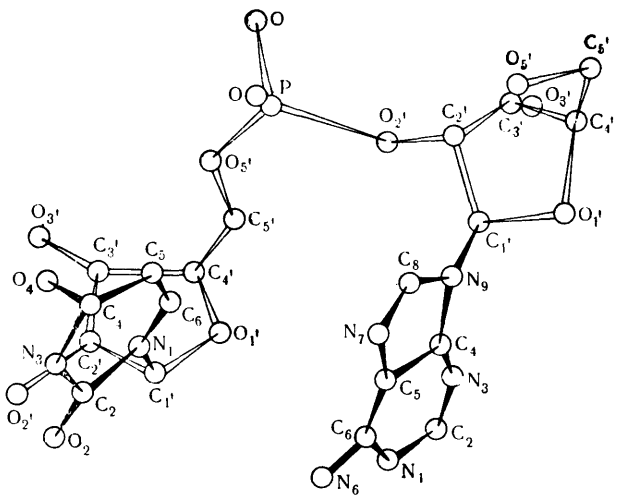


Figure 5. Model of the adenylyl-(2′–5′)-uridine molecule according to X-ray diffraction analysis[47].

Oligonucleotides have a number of specific properties: (1) on degradation of nucleotides, the intensity of ultraviolet absorption increases (hyperchromic effect) (see, for example, Refs. 1, 89, 144, and 145); (2) spectropolarimetry of oligonucleotides reveals a powerful cotton effect, which is not equal to the sum of the effects of the component mononucleotides, and the independence of the specific rotation of oligonucleotides of concentration[16,17,145–152]; (3) the circular dichroism of oligonucleotides does not agree with the sum of the effects associated with the circular dichroism of the component nucleotides[153,154]; (4) the fluorescence spectra of di- and poly-nucleotides and of the component monomers are qualitatively different[155,156]; (5) the NMR spectra of deoxyoligonucleotides reveal a shift of the proton signals from thymine relative to the mononucleotide[157].

The facts enumerated above indicate the occurrence of powerful interaction between the bases in oligonucleotides, which is shown even in dinucleotide phosphates. Several types of such interaction are possible, for example horizontal association via hydrogen bonds or vertical association as a result of π-electron interactions between the heterocyclic systems. Since dinucleoside phosphates which are derivatives of dimethylaminopurine exhibit a greater hyperchromism at all pH values than the adenine derivatives[158], it is unlikely that the interaction of the bases is determined by hydrogen bonds, particularly since it has been shown for diadenylic acid, for example, that the energy of interaction between the bases exceeds the energy of the hydrogen bond[157,159]. Furthermore, the disappearance of hyperchromism in dinucleotides such as adenylyl-(3′–5′)-uridine and adenylyl-(3′–5′)-cytidine 3′-phosphate on saturation of the 5,6-double bond by hydrogenation[160] or photolysis[161] demonstrates the important role of the π-electron systems of the bases in their interaction.

Finally, the study of aqueous solutions of mononucleotides, nucleosides, and purine and pyrimidine bases by NMR spectroscopy[162–165], osmometry[166,167], and ultracentrifugation[169] revealed a high degree of association of their molecules. It was then established that the interaction between the purine derivatives is favoured more than the interaction between purine and pyrimidine derivatives and the latter is in turn favoured more than the interaction between pyrimidine derivatives. On this basis, it was concluded that the mechanism of association consists in the arrangement of the bases in a pile, one on top of the other, as a result of the hydrophobic interactions between the π-electron systems of the bases. It is interesting that guanosine 3′- and 5′-phosphates and isoguanosine [6-amino-2-hydroxy-9-(β-D-ribofuranosyl)-purine] are believed to be arranged in a pile in the form of hydrogen-bonded tetramers with generation of a spiral ordered structure, which leads to the formation of a gel[169–175].

Association complexes of monomers in solution are not broken down by water molecules. This is explained by the presence of strong water–water hydrogen bonds. On the other hand, in dimethylformamide and in dimethyl sulphoxide such hydrogen bonds are not formed because of the absence of proton donors in the molecules of these solvents. However, since they are proton acceptors, they form hydrogen bonds with the molecules of the solute, breaking down its ordered structure[163].

The interaction between bases takes place, and actually to a greater extent than between monomers, in oligo- and poly-nucleotides. In these substances the interaction between the π-electrons of adjacent rings essentially gives rise to a new electronic system, which in fact determines the specific optical properties of the entire molecule[1,176,177].

The study of homogeneous oligo- and poly-nucleotides substituted in the heterocyclic ring (see, for example, Refs. 159 and 178–187) showed that the stability of the secondary structure of polymers increases somewhat on substitution, although at the same time the capacity for the formation of a double spiral with a complementary chain may be reduced. Probably hydrophobic interactions rather than hydrogen bonds play a decisive role in the stabilisation of the secondary structures of DNA and RNA (see, for example, Refs. 187 and 188 and also Tikhonenko's review[189])†.

†This review does not deal with the interactions between bases arising as a result of the formation of hydrogen bonds in accordance with the complementarity principle, since there is an extensive literature, including reviews, on this question, closely related to the study of the structure and functions of nucleic acids, which is outside this scope of the problem discussed here.

The significant role of hydrophobic forces and the stabilisation of the secondary structure of polynucleotides is also indicated by the observed association of purines with dinucleotides[190]: probably purine penetrates the dinucleotide molecule between the bases of the latter and, as a result of π-electron interaction with each of these, it, as it were, draws them together, forming a structure similar to a three-layer sandwich. In this connection there is an interesting hypothesis[191] that the possible cause of the biological activity of the notorious drug thalidomide is its similarity to nucleosides as regards capacity for hydrophobic interactions, as a result of which the thalidomide molecule may penetrate between the bases of DNA, altering its secondary structure.

11. DINUCLEOSIDE PYROPHOSPHATES AND NUCLEOTIDE COENZYMES

Evidently the interaction of the π-electron systems of the bases can also occur in P^1P^2-dinucleoside pyrophosphates. In addition, since the pyrophosphate link is more flexible than the phosphate link, it probably ensures a closer approach and maximum overlapping of the bases, which is reflected in larger hyperchromic effects of these compounds compared with dinucleotides[150,163].

An analogous phenomenon is observed also for other dinucleoside pyrophosphates, in particular the nucleotide coenzymes (flavine-adenine dinucleotide, nicotinamide-adenine dinucleotide). In the hydrolytic or enzymic dissociation of the pyrophosphate bond in FAD and NADH the ultraviolet absorption increases[192-197], which is evidence of interaction between the bases. This is confirmed also by fluoroscopic data. It has been found that nicotinamide forming part of reduced NAD fluoresces not only at 340 nm, as in the free state, but also at 260 nm,[198-201] the fluorescence being quenched by the addition of methanol to the solution of NADH.[202] On the other hand, the riboflavin forming part of FAD fluoresces more weakly than in the free state[203]. Furthermore the fluorescence of riboflavin is quenched on addition to its solution of purines[204-206], phenols[207], and chlorotetracycline[208]. By analogy with oligonucleotides, it was suggested that the interaction of the π-electron systems of adenine and the reduced nicotinamide or riboflavin is accompanied by an energy transfer[195,202,205] (see also Beinert's review[209]). The formation of such a complex is confirmed by spectropolarimetry[210,211] and NMR spectroscopy[212,213], and it has been shown at the same time that the π-complex form of NADH may be in equilibrium with an uncoiled form and that in certain enzymic reactions complete uncoiling of the coenzyme molecule takes place[213] (see Fig. 6).

The hypothesis of the π-electron nature of the interaction between the bases in nucleotide coenzymes is supported also by certain results of studies on their analogues: energy transfer, albeit much less effective than for NADH, has been observed for nicotinamide-uracil dinucleotide[214] and nicotinamide-phenol dinucleotide[215], while for nicotinamide-purine dinucleotide[216], nicotinamide-6-(β-hydroxyethylamino)purine dinucleotide[217], and nicotinamide-α-adenine dinucleotide[218] energy transfer almost as effective as for NADH has been observed. However, on the other hand, the absence of fluorescence in reduced nicotinamide-hypoxanthine dinucleotide[219] and the decrease of the fluorescence on alkylation of riboflavin in FAD at N_3 [220-222] may be regarded as evidence in favour of a considerable role of hydrogen bonds in the intramolecular association of the bases in nucleotide coenzymes.

It is most likely that intramolecular complexes in NADH and FAD are due to the interaction of the π-electron systems of the bases and are stabilised by hydrogen bonds.

An intramolecular complex, in the formation of which hydrogen bonds play the main role, is formed in nucleotide coenzymes of another type—nucleoside diphosphate sugars.

Examination of various natural NDPS [223,224] revealed a definite correspondence between the structure of the heterocyclic base and that of the residue of the nucleoside monosaccharide. Furthermore, there is a relation between the nature of the nucleotide residue in the NDPS and the type of biochemical reactions in which the NDPS is involved[223,224]. Since the NDPS react via the non-nucleoside monosaccharide residue, it was suggested that the specificity of the biochemical properties of NDPS is associated with the conformation of the monosaccharide, which in turn is determined by the structure of the nucleoside. The nucleoside residue may affect the structure of the monosaccharide residue as a result of the formation of intramolecular bonds with the latter, hydrogen bonds being the most likely. The equatorial orientation of the hydroxy-groups at the $C_{2''}$ and $C_{3''}$ atoms of the monosaccharide observed in all NDPS suggested that such bonds may arise between the –NH–CO–group in positions 3 and 4 of the base and the hydroxy-groups at the $C_{2''}$ and $C_{3''}$ atoms of the sugar (see, for example, Fig. 7). For uridine diphosphate sugars, there is also a possibility of a hydrogen bond between the 2-oxo group of the base and the 2′-hydroxy-group of ribose, as in other uracil ribonucleotides (see above).

The study of the activity of various synthetic analogues of uridine diphosphate glucose in enzymic reactions typical

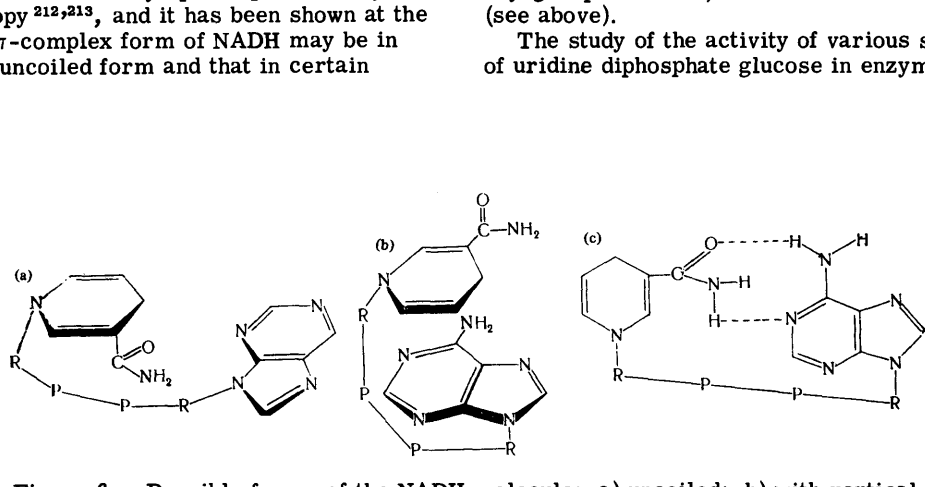


Figure 6. Possible forms of the NADH molecule: a) uncoiled; b) with vertical association of the bases; c) with hydrogen bonds[213].

for it[225-230] confirms the hypothesis that the specificity of biochemical reactions with participation of NDPS is determined by the steric structure of the NDPS molecule, since all the active analogues of UDPG contain the same grouping NH–C=O (or NH–C=S) in positions 3 and 4 of the heterocycle and consequently they can form similar intramolecular complexes.

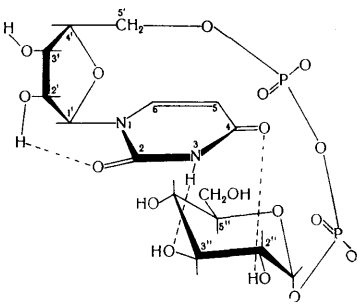


Figure 7. Schematic representation of the steric structure of the UDPG molecule[223].

The hypothesis of an intramolecular bond between the heterocycle and the sugar in NPDS was confirmed chemically by studying the rate of the catalytic hydrogenation (rhodium on alumina) of the carbon–carbon 5,6-double bond in UDPG and UMP-5'.[217] The considerable retardation of the reaction involving UDPG compared with UMP may be regarded as evidence for a significant difference in the steric accessibility of the double bonds in these compounds for the addition of hydrogen or for fixation on the surface of the catalyst, in consequence of their conformational differences. Similar results were obtained for 6-aza-UDPG and 6-aza-UMP, while *N*-methyl-UDPG, CDPG, and 2'-deoxy-UDPG are hydrogenated at the same rate as the corresponding nucleoside monophosphates[231]. The decrease of the differences in the rate of hydrogenation of UDPG and UMP in the presence of 7 M urea may be due to the breakdown of the hydrogen bond, which weakens the specific steric structure of the molecule[231].

The interaction of the base with the part of the molecule remote from it takes place in NDPS, as in FAD and NADH, because of the presence of the diphosphate unit which is fairly flexible due to the freedom of rotation characteristic of single bonds. A similar unit is present also in other nucleotide coenzymes, including nucleoside di- and triphosphates, among which adenosine 5'-diphosphate (ADP) and adenosine 5'-triphosphate (ATP) undoubtedly merit the greatest attention. Szent-Györgyi put forward the hypothesis[232] (see also later textbooks translated into Russian[233,234]) that the ADP molecule is "folded" in such a way that the terminal phosphate groups are in the immediate vicinity of the N_6 and N_7 atoms of adenine, forming with the latter a tetradentate chelate compound, using Mg^{2+} as a connecting link. A number of indirect infrared[235-237] and ultraviolet[238] spectroscopic and spectropolarimetric[239-240] data have been interpreted as favouring this hypothesis, so that it received wide recognition and the structure proposed by Szent-Györgyi for ATP may be found in many textbooks and reviews (see, for example, Refs. 241 and 242). Nevertheless the attempts to obtain direct proof of the interaction between Mg^{2+} and adenine were unsuccessful[243-252], although there is no doubt that a complex of Mg^{2+} with the phosphate group is really formed[243-255] (see also Bock's review[256]). In this connection it is suggested that in ADP and ATP the phosphate groups (via Mg^{2+}) and adenine form separate bonds with enzymes[244,256,257]. At the same time it should be noted that NMR spectroscopic data for ATP complexes with divalent zinc[245,247] and copper[245,246] ions are not inconsistent with the structure of the type proposed by Szent-Györgyi, i.e. a chelate complex of the metal ion with the nitrogen atoms of adenine and two phosphate groups, and it has been found that for the zinc complex the participation of the β- and γ-phosphate groups is more likely while for the copper complex the α- and β-phosphate groups are more likely to be involved. In addition, it has been established that Mn^{2+} may interact with adenine and with α-, β-, and γ-phosphate residues[245]. Probably Mn^{2+} can form complexes of different types. It is suggested that this capacity of the Mn^{2+} ion may explain why it can replace both Mg^{2+} and Zn^{2+} in enzymic reactions specific with respect to the ions of these metals[245]. The conformation of the possible complexes of ADP and ATP with metal ions is discussed in detail in other reviews[258,259].

12. INTRAMOLECULAR INTERACTIONS IN NUCLEOTIDOPEPTIDES

The amino-acid and peptide derivatives of nucleotides with a covalent bond between the fragments (nucleotidopeptides) play an important role in metabolic processes (see, for example, Refs. 260, 261). Unfortunately, from the chemical standpoint these compounds have been inadequately investigated. An exception are the nucleotidopeptides with a phosphoramidic nucleotidopeptide bond, for which the relation between the structure and chemical properties has been investigated systematically[262-268].

The polyfunctional nature of nucleotido-(P–N)-peptides and the large number of single bonds permitting a wide variety of relative positions of the individual parts of the molecule impart to the molecule a considerable capacity to assume the conformation suitable for intramolecular interactions between groups which are not directly linked. The effect of these interactions on the properties of the nucleotidopeptide bond may be very great because of the specific properties of both the phosphorus atom (capacity for p_π–d_π conjugation with atoms which are not directly linked to it) and the nitrogen atom (tendency to undergo protonation not only by the protons from the medium but also from the proton-donor groups of the same molecule).

The study of nucleotidyl-(5'–N)-amino-acids, in which the amino-acid residue does not contain additional functional groups, showed that the 5'-phosphoramidate bond in these compounds is readily hydrolysed in an acid medium and is stable in neutral and alkaline media[262-266] as in simple amides of phosphoric acid and its esters. However, in a weakly acid medium (pH 2.5–5) the hydrolytic stability of the phosphoramidate bond depends on the nature of the heterocyclic base of the nucleotide[262,263]. Examination of the structure of nucleotidyl-(5'–N)-amino-acids led to the hypothesis that the interaction of the base with the phosphoramino-acid residue takes place via hydrogen bonds, as shown in Fig. 8, for example. Although the *anti*-orientation of the base is typical for nucleotides, as shown on Russ. p. 227, it is possible that in this case (schemes a, b, and d) the energy required to overcome the barrier between the *anti*- and *syn*-regions is compensated by the formation of hydrogen bonds.

Some confirmation of the proposed structures was obtained by infrared and ultraviolet spectroscopy[262], but more detailed information about the intramolecular interactions in nucleotide-(P–N)-peptides was obtained by the study of their hydrolytic stability[262–268]. Fig. 8 shows that in the amino-acid derivative of guanosine 5′-phosphate (b) the phosphoramidate nitrogen is protonated even in a neutral medium, which probably accounts for the higher rate of its hydrolysis compared with the uridine 5′-phosphate derivative. On the other hand, adenylyl-(5′–N)-phenylalanine and uridylyl-(5′–N)-phenylalanine have similar stabilities, as was to be expected on the basis of the structures (a), (c), and (d) in Fig. 8. The decrease of the differences between the rates of hydrolysis of the phosphoramidate bond in phenylalanine derivatives of various nucleotides on raising the temperature[263] and on increasing the acidity of the medium[262,263] may be a consequence of the breakdown of specific hydrogen bonds.

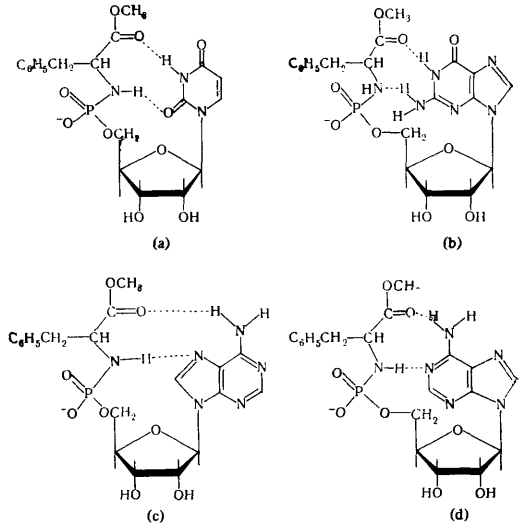
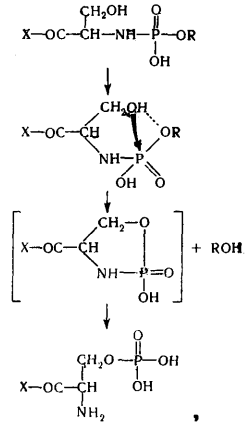


Figure 8. Schematic representation of the possible hydrogen bonds in methyl esters of uridylyl-(5′–N)-phenylalanine (a)[262], guanylyl-(5′–N)-phenylalanine (b)[263], and adenylyl-(5′–N)-phenylalanine (c)[264] or (d).

In the presence of the nucleotidopeptide molecule of other functional groups, the properties of the phosphoramidate bond can change. Thus the introduction into the 3′(2′)-position of the nucleotide fragment of an additional phosphate group leads to some stabilisation of the P–N bond, but only at a pH less than 2.5.[266] Probably under these conditions the 5′-phosphoramidate and the 3′(2′)-phosphate groups are close together, which may be favoured by the *gg*-conformation of the $C_{5'}$–$O_{5'}$ bond and the $C_{2'}$-*endo*-bending of the ribose ring. However, at higher pH this interaction breaks down as a result of the electrostatic repulsion between the dissociated phosphate groups.

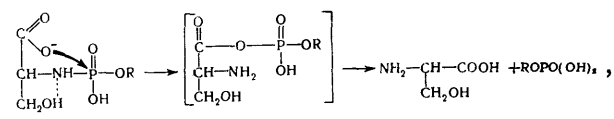
On going from amino-acid to peptide derivatives, the stability of the phosphoramidate bond also increases somewhat. The study of the rate of hydrolysis of a number of derivatives of guanosine 5′-phosphate at a pH less than 2.0 and at different temperatures led to the conclusion that the decisive factor in such increase of stability is the occurrence of steric hindrance in the protonation of the phosphoramidate nitrogen by the protons of the medium[263]. If, however, protonation takes place intramolecularly, for example with participation of the guaninine amino-group (see Fig. 8), an increase in the length of the peptide chain does not lead to any appreciable change in the stability of the phosphoramidate bond[263].

Examination of the hydrolytic stability of nucleotido-(5′–N)-peptides shows that the appreciable differences in the stability of the phosphoramidate bond are nevertheless only quantitative. However, when the peptide unit contains functional groups, there is a possibility of a fundamentally new type of dissociation of the nucleotidopeptide bond. Thus nucleotidyl-(5′–N)-amino-acids with a free carboxy-group[267] and esters of nucleotidyl-(5′–N)-serines with a free serine hydroxy-group[268] are hydrolysed on treatment with acid not only at the P–N bond with formation of the nucleotide and the amino-acid but also at the phosphoester bond with formation of the nucleoside and the phosphoramino-acid. One of the possible mechanisms of hydrolysis at the phosphoester bond includes intramolecular protonation of the phosphoramidate unit and the formation as an intermediate of a cyclic phosphoramino-acid derivative:



where ROH is the nucleoside and X is the peptide or OCH_3.

The intramolecular interaction between the hydroxy-group of serine and the phosphoramidate group is observed also in an alkaline medium, resulting in the dissociation of the phosphoramidate unit (simple phosphoramidates are stable in an alkaline medium)[268]. This dissociation takes place in different ways depending on which groups participate in the catalytic step. If this step involves the simultaneous participation of the hydroxy- and carboxy-groups, then the phosphoramidate bond dissociates (the carboxy-group may be either adjacent or remote, for example the terminal carboxy-group in the tri- and tetra-peptide derivative of the nucleotide where serine is the *N*-terminal amino-acid):

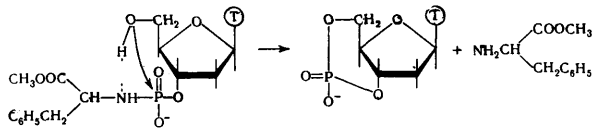


where ROH is the nucleoside.

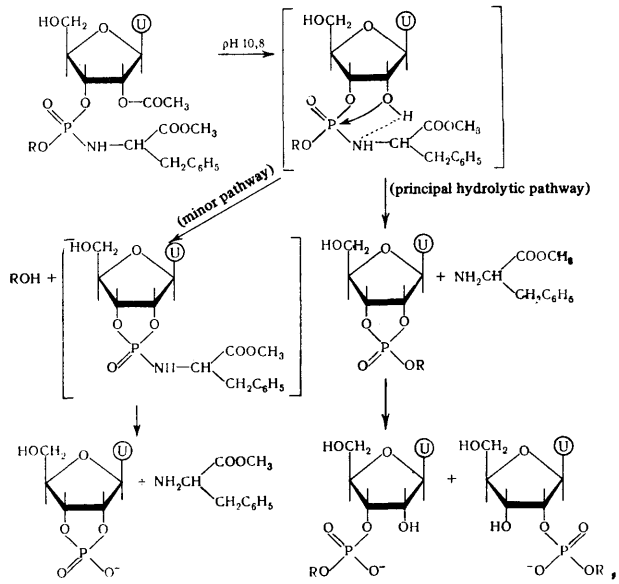
If only the hydroxy-group takes part in the catalytic step, then in alkaline degradation the phosphoester group dissociates by the acid hydrolytic mechanism described above, with formation of an intermediate five-membered cyclic phosphate, which dissociates in an alkaline medium to the *N*-phosphopeptide.

Thus a structure with a characteristic "loop" at the amino-acid end of the molecule is typical for nucleotidyl-(5′–N)-amino-acids with an additional functional group in the amino-acid fragment.

Electrophilic-nucleophilic intramolecular catalysis similar to that described above for serine derivatives of nucleoside 5′-phosphates is also observed for the thymidylyl-(3′–N)-phenylalanine ester, which on standing or brief heating in dimethylformamide is converted into thymidine 3′,5′-cyclic phosphate with simultaneous elimination of the amino-acid[143]:



In this case nucleophilic substitution at the phosphorus atom may be favoured by the conformation of the molecule in which the amide nitrogen is close to the 5′-hydroxy-group of deoxyribose (*gg*-conformation of the $C_{5'}$–$O_{5'}$ bond and $C_{3'}$-*endo*-bending of the pentose ring). An analogous intramolecular effect of the hydroxy-group favourably oriented in relation to the phosphoramidate group is most fully shown in ribonucleoside 3′-phosphoramino-acids, where the position of the hydroxyl near the P–N bond is fixed by the sugar ring. Indeed, while the amino-acid derivatives of thymidine 3′-phosphate and 5′-phosphate behave almost identically in aqueous solution regardless of the position of the phosphoramino-acid residue, being stable at pH > 3,[143] the amino-acid derivatives of ribonucleoside 3′-phosphates can exist under these conditions only if the 2′-hydroxy-group is blocked[262]. The role of the 2′-hydroxy-group in this phenomenon is confirmed by the formation of nucleoside 2′,3′-cyclic phosphate on elimination of the protective 2′-acetyl or 2′-tetrahydropyranyl groups under conditions where the isolated P–N bond is stable (pH 10.8 and 4.5 respectively)[262]. An analogous phenomenon was observed in the amino-acid derivatives of dinucleoside phosphates at the internucleotide phosphorus: while thymidylyl-(3′–5′)-thymidino-(P–N)-phenylalanine is quite stable in neutral aqueous solution, its ribo-analogue—2′-*O*-acetyluridylyl-(3′–5′)-uridino-(P–N)-phenylalanine—hydrolyses immediately after liberation of the 2′-hydroxyl:



where R = H for uridylyl-(3′–N)-phenylalanine and R is the nucleoside residue for uridylyl-(3′–5′)-uridino-(P–N)-phenylalanine.

The information obtained in the study of synthetic nucleotidopeptides suggests that, by virtue of numerous conformational possibilities, the individual fragments of the nucleotidopeptide can interact with one another. A consequence of this is extensive variability of the reactivity of nucleotidopeptides. This permits at least two conclusions. Firstly, in the determination of the types of covalent bonds in natural nucleotidopeptides one must use with great caution data obtained in the study of relatively simple structures. This is clearly shown for the phosphoramidate bond as an example, which, while stable in neutral and alkaline media in the case of simple compounds, becomes labile under the same conditions if the conformation of the molecule is such that proton-donor groups are adjacent to the phosphoramidate group. On the other hand, in the presence of functional groups capable of intramolecular catalysis of hydrolysis and sterically similar to the phosphoramidate group, anomalous dissociation of the phosphoramidate unit may occur also in an acid medium: instead of the dissociation of the phosphoramidate bond (as in simple nucleotide amides), the phosphate residue migrates from the nucleoside to the peptide. Thus, on the basis of the structure of the hydrolysis products of nucleotidopeptides, unambiguous conclusions concerning the nature of the bond in the natural compound cannot be arrived at. In the first place, the available information about the intramolecular interactions in nucleotido-(P–N)-peptides shows that even in a fairly simple molecule consisting of mononucleotide and peptide fragments there is considerable scope for self-regulation: the mutual approach of the phosphoramidic group and a proton donor or acceptor leads to an enhancement or correspondingly a decrease of its reactivity. This suggests the possibility of the existence of analogous mechanisms of the activation of the phosphate residue of mononucleotides in biosynthetic processes such as the formation of internucleotide bonds in the presence of specific enzymes. The enzyme–substrate complex of the phosphoramidate type with the appropriate conformation can effect the transfer of the mononucleotide residue to the 3′-hydroxy-group of the terminal nucleotide of the polynucleotide chain being formed. The ease of the regulation of such a process by the transfer of a proton to the phosphoramidic nitrogen or its removal makes this hypothesis very probable.

It may be expected that the study of the intramolecular interactions in more complex nucleotidopeptides, in particular in oligonucleotidopolypeptides with a specified structure (with a specified sequence of mononucleotides and amino-acids), can throw light on the most important problem of modern molecular biology—the problem of mutual "recognition" of specific nucleic acids and enzyme proteins.

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Lomonosov Moscow State University

U.D.C. 632.931.43

Insect Sex Attractants

Yu.B.Pyatnova, L.L.Ivanov, and A.S.Kyskina

The review deals with the chemical study of natural attracting substances in insects. Insect attractants have been classified in accordance with structural factors: (1) unsaturated alcohols and their acetates; (2) aliphatic acids; (3) terpene-like substances. The methods of isolation of new attractants, biological tests, proof of individuality, determination of structure, and syntheses have been described in detail. The bibliography includes 140 references.

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I. INTRODUCTION

There are more than a million species of insects in nature. Among this wide variety similar species are encountered, which are almost indistinguishable in their external features. However, in the world of insects there is almost never any crossing of different species. The maintenance of "order" in nature is favoured by a number of refined phenomena involving sight, hearing, and especially smell, which is very highly developed in insects. This enables them to find food, sites for the deposition of eggs, and also individuals of the opposite sex.

The French naturalist Jean Henri Fabre was the first to note at the end of the XIXth century that the female of *Saturnia peri* (L) placed in a cage attracted a large number of males. He carried out experiments with other species of butterflies (moths) and concluded that the female executes vibrations which are propagated in air in the form of waves and are received by the antennae of the male. Later it was established that the information provided by the female is transmitted with the aid of a chemical substance. These substances have been called sex attractants†.

Sex attractants are extremely effective biologically active compounds and are distinguished by high specificity. These properties are of great value for the investigation of practical application of attractants for the purpose of attracting and destroying insects. The application of attractants in the fight against harmful insect species has developed in recent years and already considerable successes have been achieved. The practical importance of attracting substances stimulated the study of the chemical aspects of the problem. At the present time the structures of a number of natural attractants have been established.

The known compounds have definite structural features, which permit the classification of the sex attractants into three groups according to their structures: unsaturated alcohols and their esters, aliphatic acids, and terpene-like compounds. The first group contains the greatest number of the known attractants. It is noteworthy that the acetates of unsaturated aliphatic acids containing between 12 and 16 carbon atoms function as attractants for insects belonging mainly to the order Lepidoptera. No general conclusions concerning the other two groups are at the moment possible because of the insufficiency of factual data. In the present review the authors attempted to arrange the available data systematically in accordance with the structural features discovered.

A number of reviews dealing with sex attractants have been published[3-14], but these are of a descriptive type and the chemical aspects of the problem are touched upon only briefly. Nevertheless the chemical studies on sex attractants are very interesting because of their complexity and specificity. In the present review the authors' aim was to cover the literature data up to 1968 and to elucidate most fully the problems of the chemical nature and syntheses of attractants.

II. UNSATURATED ALCOHOLS AND THEIR ESTERS

1. Attractant of the Silkworm Moth [*Bombyx mori* (L.)]

In the 1940's Butenandt and coworkers began to study the attracting substance produced in the glands in the last two segments of the abdomen of the female silkworm moth. In 1959 they succeeded in isolating the sex attractant and in determining its structure[15,16]. The starting material consisted of the glands of 500 000 females. After a number of operations, shown in Scheme (I), fractions A, B, and C were obtained, which exhibited high activity. After three chromatographic purifications on Kieselguhr and then on silicic acid and repeated recrystallisation, 6 mg of the ester of 4'-nitroazobenzene-4-carboxylic acid was isolated from fraction B. After hydrolysis the substance yielded an alcohol with LE‡ = 10^{-10} μg, which was called bombykol. A further 6 mg of the bombykol ester was obtained from fractions A and C by analogous purification.

The general formula and the molecular weight of the bombykol ester were determined by elemental analysis and ultraviolet spectroscopy. The infrared spectrum showed absorption characteristic of the C–OH group in a primary alcohol, *cis-trans*-conjugated double bonds, and a methylene chain with not less than four carbon atoms. Catalytic

† The compounds secreted by one insect in order to influence another individual of the same species and to induce in the latter definite responses are frequently called "pheromones"[1]. Kirshenblat proposed a classification of such compounds and introduced the term "telergones"[2].

‡ *LE* is the unit of attraction defined as the weight of the substance in 1 ml of the attractant solution in petroleum ether which gives rise to a response in 50% of the males tested.

hydrogenation of bombykol yielded cetyl alcohol. The position of the double bonds in the molecule was established by oxidative degradation combined with paper chromatography of the ozonolysis products [17].

The combined data obtained led to the attribution of structure (I) to bombykol:

$$CH_3(CH_2)_2\underset{(I)}{CH{=}CH{-}CH{=}CH}(CH_2)_8CH_2OH\ .$$

The geometrical configuration of the compound was established by the synthesis of the four possible isomers of compound (I) and the comparison of their physicochemical and biological properties with those of the natural substance [18,19].

The *trans*-10-*cis*-12-isomer was obtained by the Wittig condensation of hex-2-ynylidenetriphenylphosphorane (II) with the aldehyde (III). This yields a mixture of the *cis*- and *trans*-isomers (IV) in approximately equal proportions. To separate the isomers and also in other syntheses [18,19], repeated crystallisation of the urea complexes was employed. After the hydrogenation of *trans*-(IV) using Lindlar's catalyst and after reduction with lithium aluminium hydride, *trans*-10-*cis*-12-(I) was obtained:

$$\underset{(II)}{CH_3(CH_2)_2C{\equiv}CCH{=}P(C_6H_5)_3} + \underset{(III)}{O{=}CH(CH_2)_8CO_2C_2H_5}$$

$$\downarrow$$

$$CH_3(CH_2)_2C{\equiv}C{-}\underset{\underset{(IV)}{}}{CH{=}CH}(CH_2)_8CO_2C_2H_5$$

$$\downarrow$$

$$CH_3(CH_2)_2C{\equiv}C{-}\underset{H}{\underset{|}{C}}{=}\underset{H}{\underset{|}{C}}(CH_2)_8CO_2C_2H_5$$

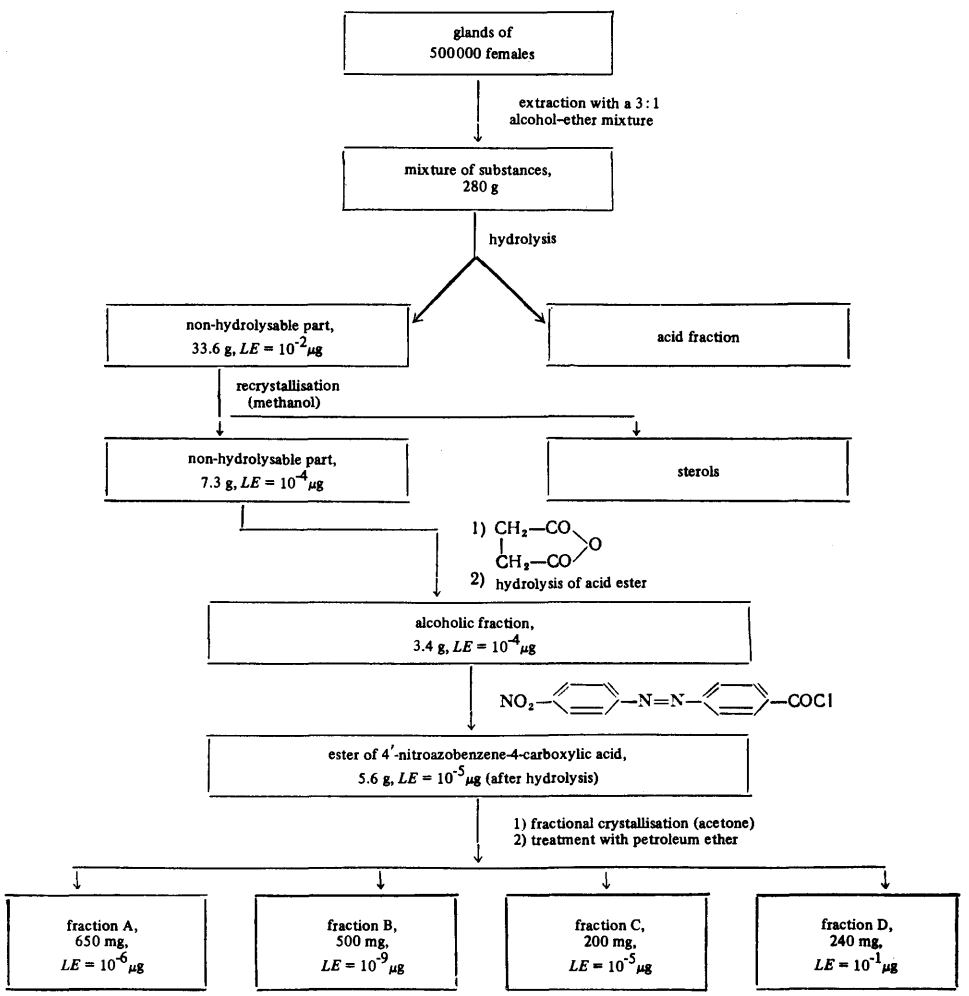
$$\downarrow\ 1)\ H_2,\ Pd/C;\quad 2)\ LiAlH_4$$

$$CH_3(CH_2)_2\overset{H}{\underset{|}{C}}{=}\overset{H}{\underset{|}{C}}{-}\overset{H}{\underset{|}{C}}{=}\underset{H}{\underset{|}{C}}(CH_2)_8CH_2OH\ .$$

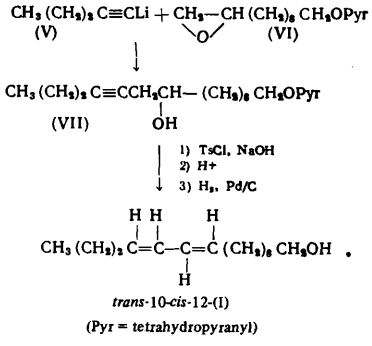
trans-10-*cis*-12-(I)

Scheme I

Isolation of the Natural Sex Attractant of the Silkworm Moth

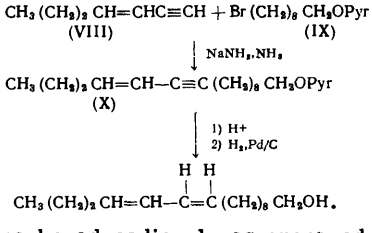


The same isomer was synthesised also by another method using the condensation of the lithium derivative of the pentyne (V) with the epoxide (VI):



After the dehydration of compound (VII), separation of the isomers, removal of the protective groups, and hydrogenation, the *trans*-10-*cis*-12-(I) isomer was obtained. The physicochemical properties of the latter were indistinguishable from those of the compound synthesised by the Wittig condensation.

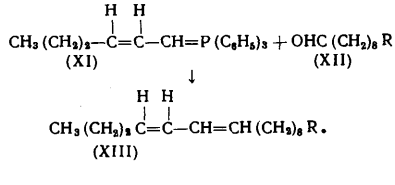
By the reaction of the sodium derivatives of *trans*- and *cis*-hept-3-enyne (VIII) with the tetrahydropyranyl ether of 9-bromononanol (IX), compound (X) was obtained, which after hydrolysis and hydrogenation by Lindlar's method gave respectively the *cis*-10-*trans*-12-(I) and the *cis*,*cis*-10,12-(I) isomers:



Trans,*trans*-hexadecadienol was prepared from *cis*-10-*trans*-12-(I) by photoisomerisation in the presence of iodine [19,9].

After comparing the melting points of the isomers and the natural bombykol, and also the melting points of the esters of 4'-nitroazobenzene-4-carboxylic acid and the ultraviolet and infrared spectroscopic data, the structure of *trans*-10-*cis*-12-hexadecadienol was attributed to bombykol. This was confirmed by comparing the activities of all the isomers in biological tests (Table 1).

Independently of these investigations, other workers [20] described the synthesis of all the isomers of compound (I). Like Butenandt, they employed the Wittig reaction, as one of the methods for the preparation of hexadecadienols:



In compounds (XII) and (XIII) R = $COOCH_3$, CH_2OCOCH_3, COOH, or CH_2OH.

Since it was shown that in the condensation process the configuration of the double bond in compound (XI) does not change, the reaction yields two isomers: *cis*-(XIII) and *trans*-(XIII). The problem of the separation of the isomers of compound (XIII) is greatly facilitated because the corresponding *cis*- and *trans*-acids differ fairly considerably in their solubility in petroleum ether and can be separated by recrystallisation [20]. This method makes it possible to obtain all four isomers.

The condensation of compounds (XIV) and (XV) was employed for the synthesis of the required *trans*-10-*cis*-12-(I), whereby it can be obtained with only a small admixture of the *trans*,*trans*-isomer:

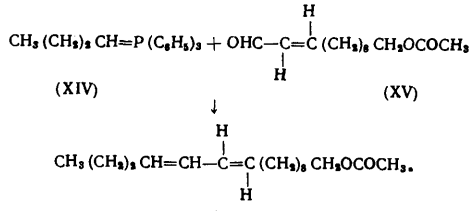
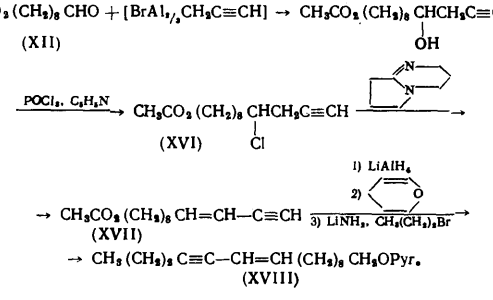


Table 1. Activity of bombykol and four geometrical isomers of a hexadeca-10,12-dienol.

Compound	*LE*, μg ml^{-1}*	*LE*, μg ml^{-1}**
Bombykol	10^{-10}	—
cis,*cis*-Hexadeca-10,12-dienol	1	—
cis-10-*trans*-12-Hexadecadienol	10^{-8}	10^{-5}
trans-10-*cis*-12-Hexadecadienol	10^{-12}	10^{-13}
trans,*trans*-Hexadeca-10,12-dienol	10	10^{3}

* According to Butenandt [19].
** According to Eiter [20].

Furthermore the same isomer of compound (I) was obtained by the following mechanism starting with compound (XII):



Dehydrochlorination of compound (XVI) yields a mixture consisting of approximately 70% of *trans*-(XVII) and 30% of *cis*-(XVII). However, after the reduction of compound (XVII) to the alcohol, protection of the hydroxy-group, and condensation with propyl bromide, mainly *trans*-(XVIII) was obtained. The biological activities of the compounds synthesised [20] differed somewhat from the activities of the isomers described by Butenandt [19] (See Table 1).

2. Attractants of the Gypsy Moth (*Porthetria dispar*).

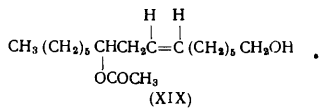
The gypsy moth causes serious damage to woods and fruit trees. After its accidental introduction in the past century into the USA, this insect multiplied rapidly and caused enormous damage in the forests of America. The gypsy moth is fairly widely distributed also in the USSR and periodically damages the forests in various regions.

It has long been known that the female of the gypsy moth attracts the male by means of "smell" and that the extract from the last two segments of the abdomen is a powerful attractant for males[21]. A benzene extract of the female abdomen is employed in the USA to control the numbers of the insects.

The first attempts to isolate the attractant were undertaken by Acree[22-24], who obtained an extract from the glands of 100 000 females and established that the non-hydrolysable fraction is active. By the chromatography of this fraction on magnesium carbonate and magnesium oxide, 12 mg of active but insufficiently pure substance was isolated, which the authors called "gyptol". Subsequently Jacobson et al.[25,26] isolated, using Acree's method[24], 75 mg of an active fraction from 500 000 females, which gave rise to five spots on paper. Only one of these was active. By extracting this spot, they obtained two substances: 3.4 mg of a solid fraction which was active at concentrations of 10^{-2} μg and 20 mg of a highly active liquid (10^{-7} μg in field tests) which fluoresced in ultraviolet light.

The reason for the existence of two natural active compounds has not been definitely established. It is suggested[26] that one of these serves to attract the male from a large distance and the other is necessary to cause it to mate.

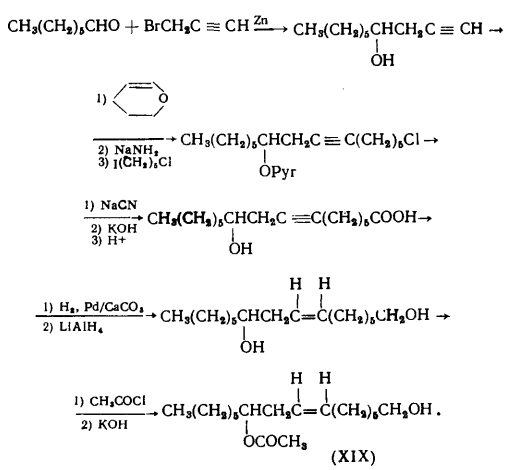
The chemical nature of the solid fraction has not been investigated. The liquid substance is optically active: $[\alpha]_D^{23} = +7.9°$. Its overall formula, $C_{17}H_{32}O_3$ or $C_{18}H_{34}O_3$, was established by elemental analysis. The infrared spectrum indicated the presence in the molecule of a primary hydroxyl, a secondary acetoxy-group, a *cis*-double bond, and a methylene chain with not less than four carbon atoms. Catalytic hydrogenation established the presence of only one double bond; its position and that of the acetoxy-group were demonstrated by oxidative degradation. As a result of these investigations, the attractant was identified as D-*cis*-10-acetoxyhexadec-7-enol (XIX):



(XIX)

Its structure was confirmed by the synthesis of the optically inactive form according to Scheme 2.

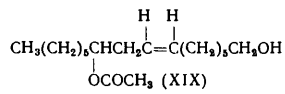
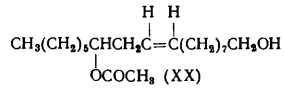
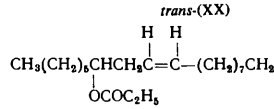
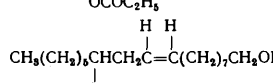
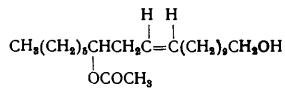
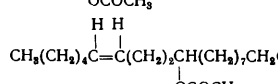
Scheme 2



DL-(XIX) was separated into the individual optical isomers[27]. The D- and L-isomers were identical in all respects, except for the sign of the angle of rotation. Nor did they differ in biological properties.

Gyptol analogues were obtained from the natural hydroxy-acids ricinoleic, (+)-14-hydroxy-*cis*-11-eicosenoic, and (+)-9-hydroxy-*cis*-12-octadecenoic by their reduction to the corresponding alcohols, acylation, and selective hydrolysis of the primary acetoxy-group[28-30] (Table 2).

Table 2. Activity of gyptol and its analogues.

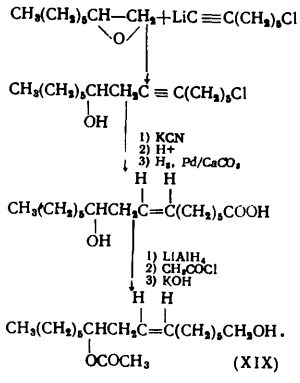
Compound	Activity, μg	
	laboratory	field
 (XIX)	10^{-12}	10^{-7}
 (XX)	10^{-12}	10^{-5}
trans-(XX)	10^{4}	$2.5 \cdot 10^{5}$
	inactive	
		
	10^{-2}	10
	inactive	

After studying the biological properties of compounds having structures similar to those of gyptol, the authors concluded that the presence of a *cis*-double bond and an acetoxy-group in β-position relative to the double bond is necessary for the activity of the molecule.

The most active analogue [compound (XX)] of the natural attractant was called "gyplure", and, because of the availability of the starting material for its manufacture, found practical application in the USA as a substitute for the benzene extract[31,32]. However, in industrial tests of the gyplure specimen the biological activity proved to be variable and in a number of cases the substance proved to be completely inactive. The authors explain this finding by the impurities produced in the preparation of gyplure under industrial conditions. In the study of this phenomenon it was found[33-35] that certain substances masked the effect of the attractant. For example, it is stated[34] that the presence of 20% of the *trans*-isomer in the highly active compound (XX) makes the latter completely inactive. An admixture of 7% of ricinoleyl alcohol also deactivates the attractant. Other workers[36,37] also note the absence of attracting capacity in gyplure specimens which they obtained by Jacobson's method[28,29]. The natural attractant (gyptol) synthesised[37] according to Scheme 3 also proved to be inactive.

The authors reject the hypothesis that in this case impurities may have masked the biological activity since the structure (XIX) of their compound was confirmed by infrared and NMR spectra. Furthermore, in tests by the electrophysiological method[38,39] of a mixture consisting of one part of the attractant obtained from Jacobson and nine parts of the synthetic substance[37], the mixture proved to be unexpectedly completely active. The reason for the loss of activity by attractants, in particular gyplure, is still not explained.

Scheme 3



(XIX)

Later a number of alcohols containing two conjugated double bonds[40] and also various unsaturated compounds incorporating a secondary acetoxy-group[41] were synthesised. Some of these alcohols, present at low concentrations, attracted insects of the order Lepidoptera. However, their activity was much lower than that of the natural attractant.

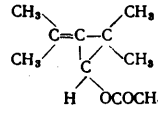
3. Attractant of the American Cockcroach [*Periplaneta americana* (L)]

Wharton and coworkers[42] isolated the active attracting substance from filter paper on which females of the black American cockcroach (*Periplaneta americana*) had been crawling and suggested that the substance was the sex attractant. The authors observed that the substance excites the male and gives rise to a characteristic behaviour of the latter. However, the amounts of attractant obtained (25 μg) were too small to establish fully its structure.

Subsequently Yamamoto[43] and Jacobson et al.[44] employed a method whereby it was possible to obtain the attracting mixture in much greater amounts and developed methods for its preparation. The methods which they proposed consist of the following steps: air was passed through a metal vessel containing about 1000 females of the American cockcroach for a period of nine months. The emerging gas stream was bubbled through a small amount of 0.1% hydrochloric acid and cooled with dry ice in a flask. The resulting condensate was extracted with hexane, the solvent was removed, and the residue was separated on a chromatographic column with silicic acid.

Thus 12.2 mg of pure attractant, consisting of a yellow liquid with a characteristic smell, was obtained from 10 000 females of the American cockcroach[44]. It gave rise to a response in the male even in an amount of 10^{-14} μg.

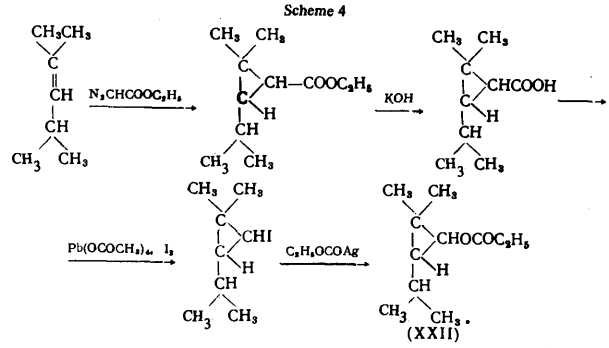
With the aid of elemental analysis, infrared and NMR spectroscopy, and chemical methods, the same authors established the structure of this substance (XXI):



(XXI)

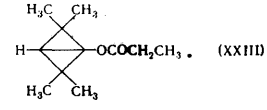
Catalytic hydrogenation of compound (XXI) yielded a substance which was identical with the dihydro-derivative (XXII), which was synthesised as indicated in Scheme 4.

Scheme 4



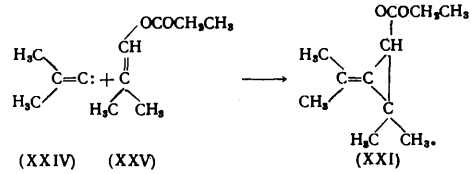
(XXII)

Jacobson's communication[44] attracted the interest of many chemists in different countries. Attempts were made to find methods of synthesis of compound (XXI) and its analogues[45-50]. Thus Day and coworkers[45] obtained compound (XXI) as one of the products of the reaction of 3-methylbuta-1,2-dienyl propionate with diazopropane followed by photolysis. The ester synthesised had the structure suggested by Jacobson for compound (XXI), but according to the NMR spectrum it differed appreciably from the natural attractant and was biologically inactive. On the basis of these data, Day and Whiting[45] suggested that the initially proposed structure for compound (XXI) is erroneous and that the bicyclobutane structure (XXIII) is more likely:



(XXIII)

Recently Wakabayashi[50] described a new synthesis of compound (XXI). The principal idea underlying the synthesis was the use of the reaction of the carbene (XXIV) with the enol ester (XXV):



(XXIV) (XXV) (XXI)

The carbene, formed in the reaction of dibromo-2-methylpropene with magnesium in tetrahydrofuran, was allowed to react with 2-methylpropenyl propionate (XXV) and gave the required product (XXI) in 18% yield. The latter had the same infrared and NMR spectra and the same gas–liquid chromatographic elution time as the substance obtained by Day and Whiting[45].

The absence of biological activity of the synthetic compound (XXI) confirms the earlier data[45] concerning its non-identity with the natural attractant.

Additional studies carried out by Jacobson and Beroza[51], who admitted that the initial structure (XXI) which they established for the sex attractant was erroneous, showed high instability of the natural compound. The crude attractant decomposes even in the cold in several days. However, in an atmosphere of nitrogen in a dilute hydrocarbon solution it can be stored at low temperatures for six months. The authors suggest[51] that compound (XXI) readily undergoes a complex rearrangement, the mechanism of which is still unknown. Thus the structure of the sex attractant of the American cockcroach requires revision.

4. The Sex Attractant of the Pink Bollworm Moth (*Pectinophora gossypiella*)

The pink bollworm moth causes considerable damage in the cotton industry. Its caterpillar, the pink bollworm, feeds on the seeds and seed filaments. All the countries in the world lose 20–25% of their cotton crop because of the pink bollworm. In the Soviet Union this variety of the insect is not widespread.

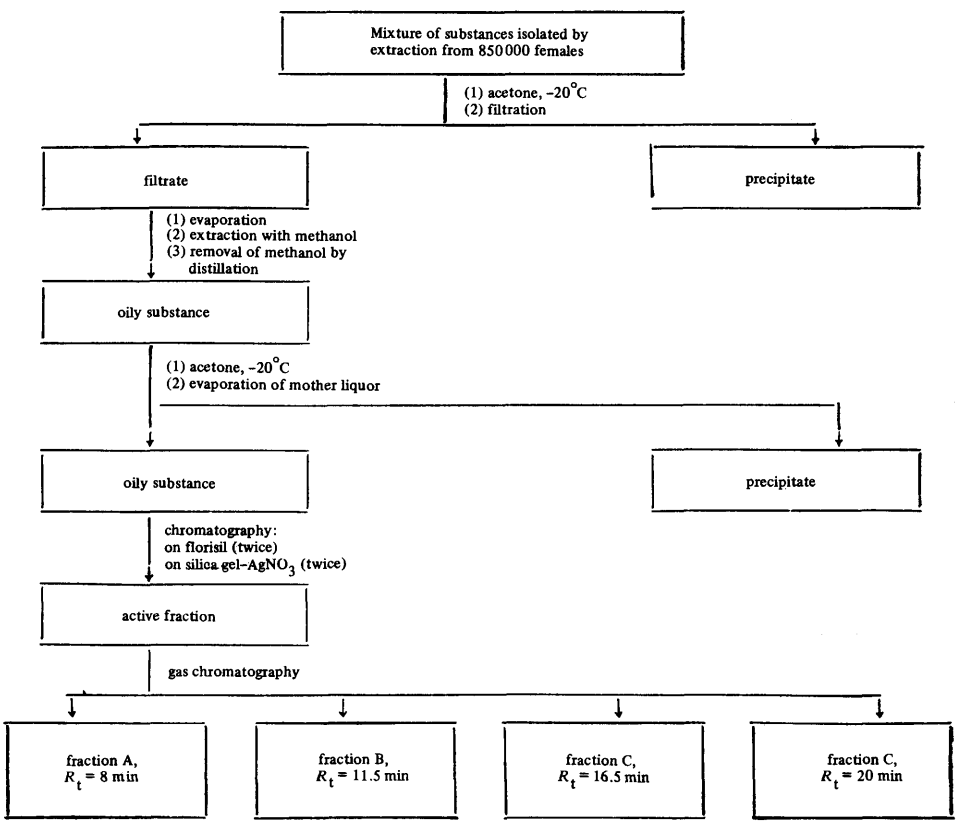
The first mention of the presence of an attractant in the females of the pink bollworm moth was made in 1957.[52] Then the characteristic behaviour of the male during mating was described[53]: excited flight, rapid wing vibration, and curving of the abdomen. A similar response was produced by an extract from the terminal segments of the female abdomen[53,54]. Such extracts were used to trap males under field conditions[54].

In 1966 the pure attractant of the pink bollworm moth was isolated and its structure was established[55]. The publication of this study is evidence of considerable progress in the chemistry of attractants. The authors, who had at their disposal 1.6 mg of the compound, established its complete structure, the investigation lasting only 2–3 years. The isolation of the sex attractant from the extract obtained from the whole bodies of 850 000 two days old females was carried out in accordance with Scheme 5.

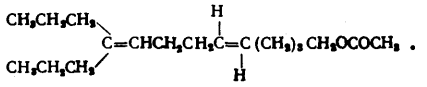
Only fraction B exhibited biological activity and was used to identify the attractant. The structure was established with the aid of physicochemical methods alone. The infrared spectrum demonstrated the presence in the molecule of a primary acetoxy-group, a *trans*-double bond, and a long methylene chain. The presence of a branched skeleton was demonstrated by means of the chromatography of the hydrogenation product[56]. The ultraviolet spectrum did not show the absorption characteristic of conjugated double bonds. Mass spectroscopy established the overall formula of the compound ($C_{18}H_{32}O_2$) and the molecular weight. These investigations suggested that the attractant is an acetate of a primary alcohol with 16 carbon atoms and has branched structure.

Scheme 5

Isolation of the Sex Attractant of Pectinophora gossypiella



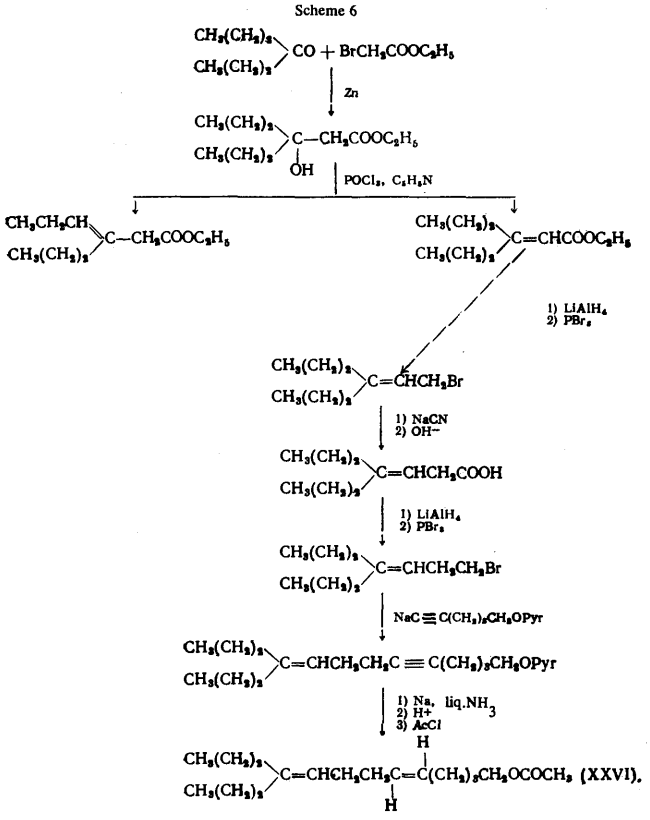
Additional NMR spectroscopic data showed that the sex attractant is *trans*-10-propyltrideca-5,9-dienyl acetate (XXVI):



(XXVI)

The structure of the attractant was confirmed by synthesis (Scheme 6) with a 0.2% yield of the final substance. The authors called compound (XXVI) "propylure" and stated that this is in fact the first natural substance with propyl branching.

Scheme 6

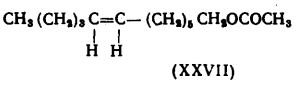


At the present time yet another method of synthesising "propylure", including a number of consecutive reactions in accordance with Scheme 7, is known.

Another cotton pest, the cotton leafworm moth [*Alabama argillacea* (Hübner)], secretes about 0.1 μg of the pheromone. A concentrate containing one tenth of this amount gives rise to a typical response in the males[57]. After the purification of the concentrate by thin-layer and gas chromatography, a substance was obtained with properties characteristic of a hydrocarbon with about 20 carbon atoms.

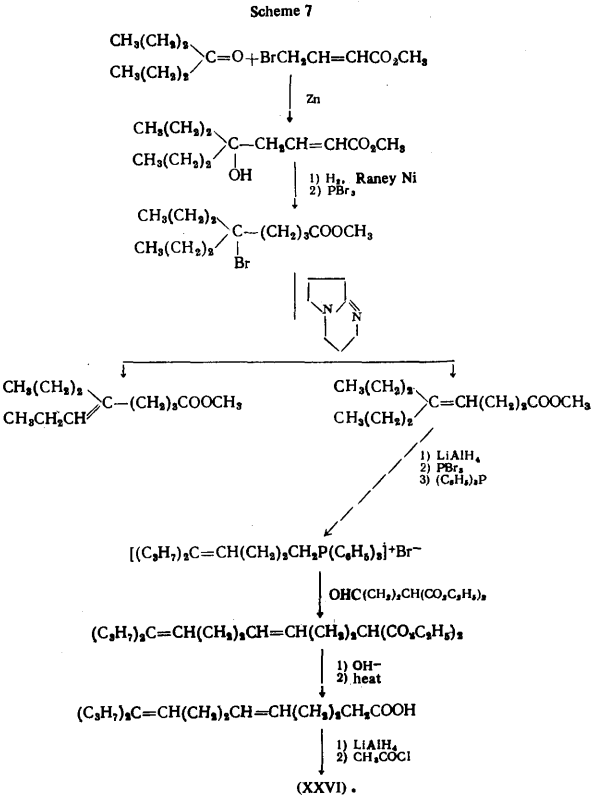
5. The Attractant of the Cabbage Looper (*Trichoplusia ni*)

The presence of a sex attractant in the females of the cabbage looper (*Trichoplusia ni*) became known thanks to the work of Ignoffo et al.[58] and Shorey[59]. In 1966 Berger[60] isolated by extraction with methylene chloride from 2500 females of the cabbage looper about 200 mg of a yellow oil containing the pheromone. The crude extract was separated from the major part of the lipids by chromatography on silicic acid, which yielded about 10 mg of a highly active substance; this, however, still contained impurities. Further purification by gas chromatography led to the isolation of the pure compound. Physicochemical methods and the chemical properties of the compound led to the determination of the structure of the attractant as *cis*-dodec-7-enyl acetate (XXVII).



(XXVII)

Scheme 7

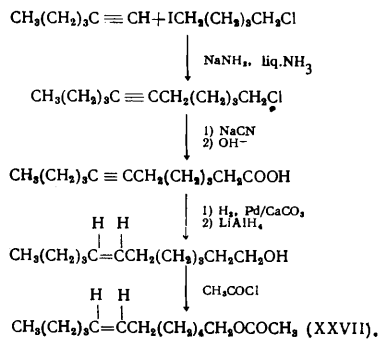


The proposed structure (XXVII) was confirmed by synthesis with an overall yield of product of 28%. The attractant was synthesised according to Scheme 8.

1-Chloroundec-6-yne (XXVII), obtained by the action of hex-1-yne and sodamide on 1-chloro-5-iodopentane in liquid ammonia, was converted into dodec-7-ynoic acid by treatment with sodium cyanide and subsequent hydrolysis. After the reduction of the triple bond in the presence of Lindlar's catalyst to a *cis*-double bond and of the carboxy-group with lithium aluminium hydride to an alcoholic group, a high yield of an unsaturated alcohol, *cis*-dodec-7-enol, was obtained. On acetylation of the hydroxy-group with acetyl chloride, the alcohol was converted into *cis*-dodec-7-enyl acetate (XXVII).

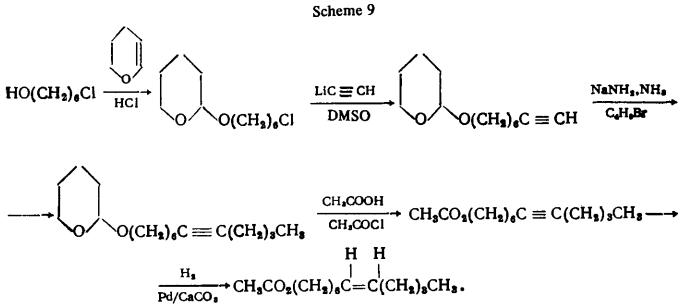
According to the infrared spectrum, the gas chromatographic elution time, and the physicochemical constants, the compound synthesised is identical with the natural attractant. The amounts of both the natural and the synthetic compounds showing the minimal biological activity are the same: 0.1 $\mu g\ ml^{-1}$.

Scheme 8



Green et al.[61] synthesised *cis*- and *trans*-dodec-7-enyl acetates by two different procedures. The method pf preparation of the *cis*-isomer (XXVII) is clear from Scheme 9 quoted below.

Scheme 9



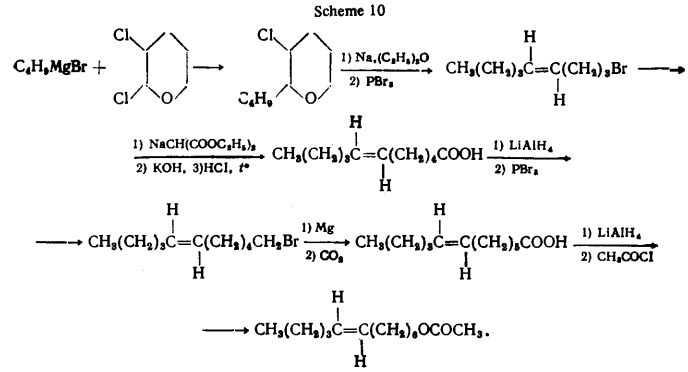
The synthesis of the *trans*-isomer according to Scheme 10 has the advantage that the final product is obtained without an admixture of the *cis*-form. The same workers and also Toba et al.[62] confirmed the high biological activity of the *cis*-acetate (XXVII) under both laboratory and field conditions. Synthetic analogues[61,63-65] of the natural attractant such as oct-7-ynyl, dodec-7-ynyl, *cis*-oct-7-enyl, *cis*-dec-7-enyl, *trans*-dodec-7-enyl, *cis*-dodec-5-enyl, *trans*-dodec-5-enyl, *cis*-dodec-9-enyl, dodecyl, and *cis*-tetradec-7-enyl acetates and the alcohols *cis*-dec-7-enol and dodecanol are weakly active or altogether inactive.

Thus the conditions necessary for the activity of the attractants of the cabbage looper are the presence of a straight twelve atom carbon chain, a *cis*-double bond in position 7, and an acetoxy-group in position 1. The failure of even one of these requirements leads to a sharp reduction or complete loss of the biological activity of the attractant.

6. Attractants of the Trinidad Butterfly (*Lycorea ceres ceres*)

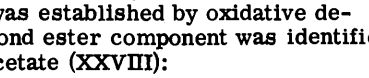
The males of the tropical butterfly of the subfamily Danainae have two organs, called androconia, which can be projected from the abdomen. During the "nuptial games" the male secretes the odorous substance through the androcones. The female attracted by the substance during the flight pursues the male.

Scheme 10



The data on the chemical nature of the substances secreted by the male moth are fewer than those of the attractants produced in the female organism. However, recently the chemical composition of the secretion of the male Trinidad butterfly (*Lycorea ceres ceres*) became known[66]. Extraction of the hairs removed from the androconia of several hundred males yielded a mixture which contained three substances according to gas–liquid chromatographic data. Adsorption chromatography of the extract from 100 males yielded two fractions: about 2.8 mg of the ester fraction and about 10 mg of the carbonyl fraction. The ester fraction was separated by preparative gas–liquid chromatography into two ester components. The infrared spectrum of one of these showed absorption characteristic of the acetate, which did not change on catalytic hydrogenation. On the basis of the mass spectra, the formula $C_{16}H_{33}OCOCH_3$ was proposed in the above investigations. The structure was confirmed by comparison with a cetyl acetate specimen.

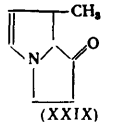
The second substance was investigated by infrared and mass spectroscopy. It was shown that it is the acetate derived from an alcohol with a molecular weight of 310, which corresponds to an unsaturated or monocyclic alcohol with 18 carbon atoms. Catalytic hydrogenation gave stearyl acetate. Comparison of the spectroscopic and chromatographic data for the compound isolated and oleyl acetate revealed a considerable similarity. The position of the double bond in the chain was established by oxidative degradation. Thus the second ester component was identified as *cis*-octadec-11-enyl acetate (XXVIII):



(XXVIII)

A synthetic specimen of compound (XXVIII) was obtained by the reduction of methyl *cis*-octadec-11-enoate with lithium aluminium hydride and acetylation of the resulting alcohol.

The unknown substance was isolated from the carbonyl fraction by vacuum sublimation. The study of the infrared, NMR, and mass spectra of this substance and a number of known compounds similar to the carbonyl component led to formula (XXIX) for the latter:



(XXIX)

The structure of the compound was confirmed by synthesis, which included the cyclisation of *N*-cyanoethyl-3-methylpyrrole[67]. The specimen obtained was identical with compound (XXIX) according to infrared, ultraviolet, NMR, and mass spectra, but it did not have the sweetish smell characteristic of the natural compound. Possibly this smell is due to traces of impurities[66]. The structure of compound (XXIX) differs sharply from that of the pheromones of the moth of this species and also from those of the attractant described earlier, but it is fairly similar to the structure of a number of plant alkaloids[68]. It is suggested[66] that compound (XXIX) is not produced in the insect organism but is introduced with the food or is derived from compounds obtained from the food.

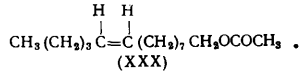
The males of another Danainae species, *Danaus gilippus berenice*, also produce an odorous secretion, which is exuded through androconia[69]. However, the chemical nature of their pheromones is still unknown.

7. Attractant of the Fall Armyworm Moth (*Spodoptera frugiperda*)

Various species of *Spodoptera frugiperda* secrete a substance which stimulates the male to mate. The substance is concentrated in the terminal segments of the abdomen. Each female produces approximately 0.01 μg of the odorous secretion[70,71].

The structure of the attractant secreted by *Spodoptera frugiperda* has now been established[72]. The terminal segments of 135 000 unmated females 3–5 days old were used for the isolation. The mixture (55 ml) obtained from the extract was separated by column and repeated thin-layer chromatography into a number of fractions. The active fractions were selected with the aid of a biological test. The final purification was achieved by preparative gas chromatography. In this way 900 mg of the pure attractant was obtained.

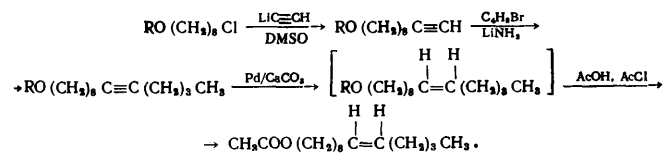
The infrared spectrum showed an absorption characteristic of the acetyl carbonyl group and a *cis*-double bond. The ultraviolet spectrum did not contain any absorption characteristic of conjugated bonds. The presence of an ester group was confirmed by alkaline hydrolysis, which resulted in complete disappearance of biological activity. On acetylating the hydrolysis product, the activity was restored. Catalytic hydrogenation yielded tetradecanol. The position of the double bond was established by ozonolysis. These investigations led to the identification of the attractant as *cis*-tetradec-9-enyl acetate (XXX)[72]:



(XXX)

Compound (XXX) was obtained from myristoleic (tetradecenoic) acid by reduction with lithium aluminium hydride and acetylation. The synthetic substance was active at a concentration of 3×10^{-12} g.

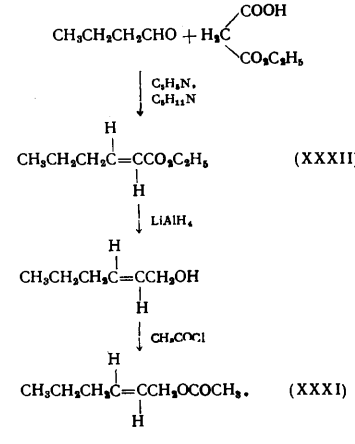
In addition, the complete synthesis of *cis*-tetradec-9-enyl acetate, based on the condensation dec-1-yn-10-ol with butyl bromide, has been described[73]:



Jacobson and Harding[74] suggested that *cis*-tetradec-9-enyl acetate be obtained using as the starting material the commercial preparation of dodec-7-enyl acetate—the attractant of *Trichoplusia ni*.

8. The Attractant of the Giant Water Beetle [*Belostoma indica vitalis* or *Lethocerus indicus* (Lep)]

The giant water beetle is a large insect approximately 7 cm long and 4 cm wide. It lives in ponds in South East Asia, Africa, and South America. The males have two tubes about 4 cm long on the abdomen. Through these the giant water beetles secrete approximately 0.02 ml of a transparent liquid with a cinnamon smell. In Southern Asia it is used as a spice in food. This liquid is probably the sex pheromone of the male[75]. Butenandt investigated the attractant of the giant water beetle[75]. To obtain the substance, he removed the glands from the male and squeezed the secretion from them. In this way he managed to secure 3 ml of the liquid. It was established by chemical reactions that the attractant is an acetate ester. The alcoholic component characterised as the 4′-nitroazobenzenecarboxylate ester[76], was found to be an unsaturated alcohol $C_6H_{11}OH$. The position of the double bond was determined by oxidative degradation. Thus it has been established that the main component of the secretion of the giant water beetle is *trans*-hex-2-enyl acetate (XXXI). This structure is confirmed by the synthesis of compound (XXXI) based on butyraldehyde and the half-ester of malonic acid. The ester (XXXII) formed on condensation was reduced to the alcohol with lithium aluminium hydride and acetylated:



(XXXII)

(XXXI)

III. ALIPHATIC ACIDS

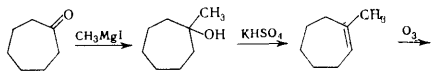
1. Attractants of the Honey Bee [*Apis mellifera* (L.)]

The complex life of the beehive is probably regulated and controlled by many pheromones having different purposes. At the present time at least several such compounds, produced by the queen and worker bees, are known. In 1959 Butler[77] showed that the secretions of the queen bee contain a pheromone which prevents the laying of eggs by the worker bees and the growth of new queens. This substance was isolated[78-81] and proved to be *trans*-9-oxodec-2-enoic acid. The studies carried out by Gary[82] provided the experimental proof of the existence of volatile sex attractants in the queen bee. The secretions of the mandibular glands of the queen enable the drones to find it during the nuptial fight. It was shown[81] that the scent attracting the drones is mainly due to 9-oxodecenoic acid. 9-Hydroxydecenoic acid accompanying it is only weakly active with respect to drones—it is responsible for the stabilisation of the swarm.

The practical and theoretical interest in the discovery of the pheromones of bees led over a short period of time to a number of independent investigations of the synthesis of *trans*-9-oxodec-2-enoic acid[79,86-92] (XXXIII), the biologically similar *cis*-isomer[93], and 9-hydroxydecenoic acid[80-91].

Among the methods described for the preparation of compound (XXXIII), the elegant synthesis from cycloheptanone[84,85] and the relatively simple synthesis, yielding compound (XXXIII) in large (of the order of 50–100 g) amounts, from glutaric aldehyde[90,91] are noteworthy.

When methylmagnesium iodide is allowed to act on cycloheptanone, 1-methylcycloheptanol is obtained, its dehydration over potassium hydrogen sulphate yielding 1-methylcycloheptene. Treatment with ozone with subsequent degradation of the ozonide yields 7-oxo-octanal, the condensation of which with malonic acid in pyridine gives after decarboxylation and purification 9-oxodecenoic acid in 20% yield:



$$\rightarrow CH_3C(CH_2)_5CHO \xrightarrow[C_5H_5N]{CH_2(COOH)_2} CH_3C(CH_2)_5CH{=}CHCOOH.$$

(XXXIII)

In another method glutaric aldehyde is converted by the Wittig reaction into the methyl ester of 2-formylhept-7-enoic acid (XXXIV):

$$OHC(CH_2)_3CHO + (C_6H_5)_3P{=}CHCOOCH_3 \rightarrow OHC(CH_2)_3CH{=}CHCOOCH_3.$$

(XXXIV)

The resulting ester (XXXIV) can be converted into the acid (XXXIII) in two ways:

(a) XXXIV $+ CH_3COCH_3 \xrightarrow{C_5H_{11}N\cdot CH_3COOH} CH_3COCH{=}CH(CH_2)_3CH{=}CHCOOCH_3 \rightarrow$

$$\xrightarrow[2)\ Na_2CO_3]{1)\ H_2;\ Pd/C} CH_3CO(CH_2)_5CH{=}CHCOOH.$$

(XXXIII)

(b) XXXIV $+ HC{\equiv}CCH_2Br \xrightarrow[Al]{Zn} HC{\equiv}CCH_2CH(OH)(CH_2)_3CH{=}CHCOOCH_3 \rightarrow$

$$\xrightarrow[HgSO_4,\ 2HgO]{1)\ H_2SO_4} CH_3COCH{=}CH(CH_2)_3CH{=}CHCOOCH_3 \rightarrow$$

$$\xrightarrow[2)\ Na_2CO_3]{1)\ H_2,Pd/C} CH_3CO(CH_2)_5CH{=}CHCOOH.$$

(XXXIII)

The *cis*- and *trans*-isomers are isolated by crystallisation from the mixture of 9-oxodecenoic acids. It is interesting that a considerable amount of 10-hydroxydec-2-enoic acid was detected in the food received by the queen[94]. The biochemical role of this acid is still not completely clear, but its bactericidal, fungicidal[95], and anti-tumour[96] properties are already known. The synthesis of this compound has also been worked out in detail[87,89,97-100].

In addition to *trans*-9-oxodecenoic and 9- and 10-hydroxydecenoic acids, a large number of carboxylic acids were also isolated from the queen bee extract and from the royal jelly. Thus nonanoic, decanoic, dec-2-enoic, *p*-methoxybenzoic, 9-oxodecanoic, 9-hydroxydecenoic, *p*-hydroxybenzoic, decane-1,10-dicarboxylic (sebacic), dec-2-ene-1,10-dicarboxylic, adipic, pimelic, and suberic acids in the form of their methyl esters and phenylacetic and phenylpropionic acids have been found and identified[80]. In addition there remain unidentified[80] a further 17 peaks, detected by the gas chromatography of the acid fraction of the royal jelly. Aromatic acids are frequently encountered in nature in many tissues and probably do not play a specific role in bees. On the other hand, the majority of the aliphatic acids isolated have a chain with ten carbon atoms. This situation is scarcely fortuitous. Members of this series of acids may be biogenetically related, constituting the units of a single series of reactions in the living organisms. However, their biochemical role and interrelations have not been adequately investigated.

2. The Attractant of the Black Carpet Beetle [*Attagenus megatoma* (Fabricius) or *Attagenus piceus* (Olivier)]

The attractant of the black carpet beetle was recently isolated and identified[101,102]. The active substance was found in the acid fraction of the extract from 30 000 females. After purification by adsorption and gas–liquid chromatography, the methyl ester of an unknown acid was isolated by three gas-chromatographic purifications.

The structure of the acid was established solely by physicochemical methods. The molecular weight and the general formula of the compound ($C_{15}O_{26}H_2$) were obtained with the aid of the mass spectrum. The infrared spectrum indicates the presence in the molecule of a carbonyl group, conjugated double bonds having the *cis*,*trans*-configuration, and a methylene chain. The ultraviolet spectrum confirmed the presence of a conjugated diene system.

The NMR spectrum confirmed the spectroscopic data. On the basis of these studies, the esterified attractant of the black carpet beetle could be identified as one of the two *cis*,*trans*-isomers of methyl tetradeca-3,5-dienoate (XXXV):

$$CH_3(CH_2)_7CH{=}CH{-}CH{=}CHCH_2COOCH_3.$$

(XXXV)

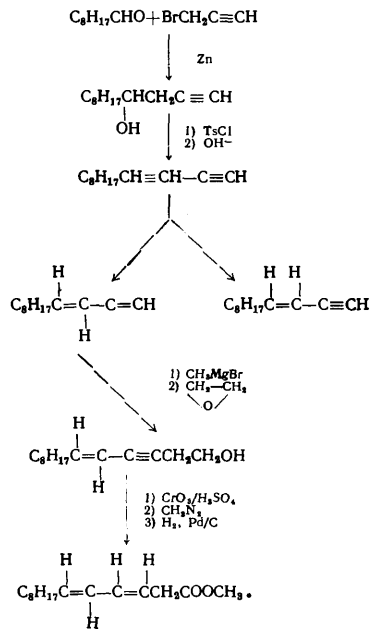
The geometrical configuration of the compound was established by synthesising the two isomers and comparing their physicochemical properties. Methyl *trans*-3-*cis*-5-tetradecadienoate was obtained by the method devised for the synthesis of methyl *trans*-3-*cis*-5-tridecanoate[103]. The *cis*-3-*trans*-5-isomer (XXXV) was synthesised according to Scheme 11.

The synthetic *trans*-3-*cis*-5-isomer (XXXV) had the same spectroscopic and chromatographic properties as the natural compound, while the *cis*-3-*trans*-5-isomer showed considerable differences in the infrared and NMR spectra. Therefore the structure of the *trans*-3-*cis*-5-tetradecadienoic acid was attributed to the compound. The response of the male to the synthetic substance was somewhat weaker than to the extract from the female. The authors suggest that[102] the extract might contain other active components, which were lost during isolation.

3. Attractant of the Sugar-beet Wireworm [*Limonius californicus* (Mann)]

The sugar-beet wireworm is a widespread pest on sugar-beet, potatoes, onions, and other crops. Its larvae live and develop in the soil on the roots of the plants, which makes the fight against them difficult. The adult insects crawl out on the surface of the earth in the spring for a brief period of mating. It was noted[104] that each female may attract a large number of males. Lilly[105] showed that this attraction is due to the sex pheromones produced by the female.

Scheme 11



In paper chromatographic experiments using a mixture of ethanol and ammonia (95 : 5) the alcoholic extract of the abdomens gave a spot with $R_f = 0.85$, which attracted the males under laboratory conditions.

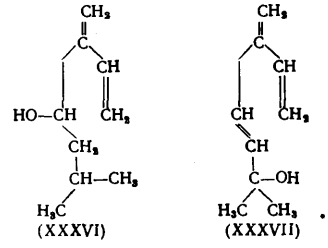
In his latest work Lilly[106] stated that he succeeded in isolating and identifying the sex attractant of the females. It proved to be n-valeric acid. The biological activities of synthetic n-valeric acid and the natural attractant were the same.

The female of the wireworm *Limonius canus* (Le Conte) also secretes a sex attractant[107] which gives rise to a response in the males when present in an amount equivalent to 0.005 of the total substance secreted by one female. According to preliminary data, the pheromone is a carboxylic acid.

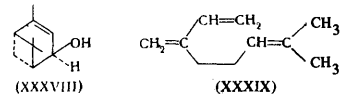
IV. TERPENE-LIKE COMPOUNDS

1. Attractant of the bark beetle (*Ips confusus*)

The males of the bark beetle bore passages in coniferous trees and produce a brown powder (a mixture of wood particles and excrement) which contains pheromones[108]. The powder attracts both sexes, especially females. A mass attack by the beetles due to the presence of these pheromones frequently results in the destruction of the tree. In biological tests an appreciable response of the female was obtained with the substance from the benzene extract corresponding to 3×10^{-8} g of the powder[108]. A highly active fraction[108] of pheromones was obtained in a yield of 0.0007% (relative to the weight of the initial powder) from 3 kg of the powder derived from 21 000 males by extraction, vacuum distillation, and gas chromatography. Nonanal, geranyl acetate, and two terpene alcohols, (XXXVI) and (XXXVII), hitherto not described in the literature were obtained from this fraction:



Apparently nonanal and geranyl acetate are impurities. It is not known whether the terpene alcohols (XXXVI) and (XXXVII) are of plant origin or metabolic products of the beetles. Subsequently (-)-2-methyl-6-methyleneoct-7-en-4-ol (XXXVI), detected previously, and two other terpene alcohols,



were isolated[109] from 4.5 kg of the powder produced by the males of *Ips confusus*. The structures of compounds (XXXVI), (XXXVIII), and (XXXIX) were established by physicochemical methods and confirmed by synthesis.

In laboratory biological tests compounds (XXXVI), (XXXVIII), and (XXXIX) were inactive[109] in amounts of 1000, 20, and 100 μg respectively. At the same time a mixture of 1 μg of compound (XXXVI) with 0.01 μg of compound (XXXVIII) and a mixture of 1 μg of compound (XXXVI) with 1 μg of compound (XXXIX) gave rise to a typical response by the beetles.

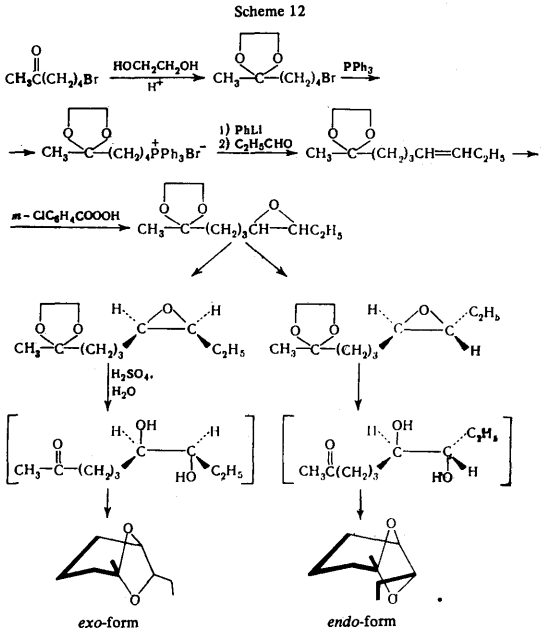
Tests under field conditions showed[110] that the most active is a mixture of compounds (XXXVI), (XXXVIII), and (XXXIX), which caused the appearance of 14 males and 18 females during 20 min (average per day). A mixture of compounds (XXXVI) and (XXXIX) attracted only the females. The individual compounds and their other combinations attracted only a few isolated insects.

An interesting and unexpected observation was made[110] that compound (XXXVI) and also its mixture with compound (XXXVIII) attracted *Ips latidens*. The addition of 0.1 μg of compound (XXXIX) to a mixture of 2 μg of compound (XXXVI) with 0.1 μg of compound (XXXVIII) greatly reduced the attraction of *Ips latidens*, but greatly enhanced the attraction of *Ips confusus*. The unusual synergistis system obtained by the addition of compound (XXXIX) to a mixture of compounds (XXXVI) and (XXXVIII) the attractive properties in relation to *Ips latidens* and enhances them in relation to *Ips confusus*.

Recently the structure of the sex attractant secreted by *Dendroctonus brevicomis* [western pine beetle (Ed. of Translation)] has become known[111]. The concentrate of the active substance was isolated from the brown powder. The pure

substance was obtained by column and gas–liquid chromatography. The study of the spectroscopic and chemical properties of the compound isolated established that it has the structure of a cyclic ketal. It was shown by the synthesis of *exo*- and *endo*-7-ethyl-5-methyl-6,8-dioxabicyclo[3,2,1]-octane (Scheme 12) and by comparison of the synthetic substances with the natural specimen that the attractant, which was called brevicomin, is the *exo*-form of the above compound. It is interesting that similar cyclic structures are rare among natural compounds.

Scheme 12



In the study of the biological activity it was shown that, as in the synergistic phenomenon observed for the attractants of *Ips confusus* [109], certain inactive natural fractions enhance the activity of brevicomin.

Another pest on conifers in which a sex attractant was detected, is the introduced pine sawfly [*Diprion similis* (Hartig)]. In 1960 Coppel et al.[112] noted that the unfertilised females of the introduced pine sawfly attract a large number of males under field conditions. Extraction of the filter paper on which the females of this species had been crawling followed by purification using preparative chromatography led to the isolation[113] of a concentrate containing as its main component the sex attractant of the female. This compound proved to be entirely stable. Thus it did not change at 100°C over a period of 5 h and lost its biological activity only at 180°C after 2 h. Recently Casida and coworkers[114] stated that, having modified Jamamoto's procedure[43] for the collection of the sex attractant of the American cockcroach (*Periplaneta americana*), they succeeded in isolating the fraction of the attractant of the introduced pine sawfly in greater amounts and contaminated to a smaller extent than in the isolation by earlier methods. Nevertheless the inadequate purity of the compound obtained precluded final conclusions concerning its structure.

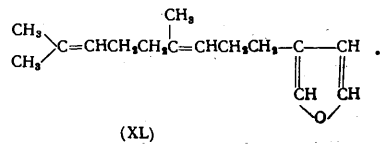
2. Pheromones Causing a Response of Fear or Defence

In social insects (ants, bees) a "chemical language" is fairly highly developed. Apart from the already known functions of attraction, these insects must have a means of communication with one another. There are a number of substances with the aid of which social insects communicate danger, indicate the direction to sources of food, mark their trail in order to return to the nest, etc.

A fairly large number of fear-inducing pheromones, secreted by various species of ants, are known at the present time. Frequently the response of ants to the same compounds is different depending on their concentration in air. Substances which when present in high concentrations give rise to a fear response, for example, at low concentrations attract the working individual.

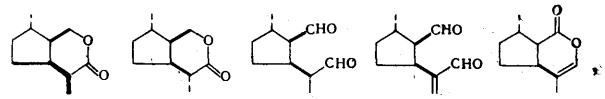
Most species of ants secrete formic and acetic acids which act as repellents. Some species secrete a mixture of acetic, propionic, and isovaleric acids[115]. The West African black ant *Crematogaster* (*Atopogyne*) *africana* (Mayr) emits a characteristic smell when alarmed. It was established[116] that the smell is due to hex-2-enal, which acts as a repellent. The same compound is secreted as a repellent by the cockcroach *Eurucotis floridana*[117].

The ant *Lasius fuliginosus* secretes a substance which causes the excitation of this species but is toxic to other ants. Its active component is dendrolasine[118] (XL):



(XL)

The pheromones of ants of various species of the genus *Iridomyrmex* and *Dolichoderus* have now been fairly well investigated. Thus it has been established[119–121] that the ants *Iridomyrmex detectus*, *I. humilis*, and *I. nitidus* secrete iridomyrmecin (XLI), isoiridomyrmecin (XLII), iridodial (XLIII), and isodihydronepetalactone:



(XLI) (XLII) (XLIII) (XLIV) (XLV)

Dolichodial (XLIV) was found in the secretion of the ant *Dolichoderus acanthoclinea* Clarki[122,123]. These compounds belong to the class of cyclopentanoid monoterpenes, since they are biogenetically related to terpenes[115]. 2-Methylhept-2-en-6-one, 2-methylheptan-4-one, 4-methylhexan-2-one, and 4-methylheptan-3-one, secreted by ants of various species, also have a terpene-like structure[115,124]. It is interesting that the structure of compounds (XLI) and (XLIV) closely resemble those of substances isolated from plant sources, in particular from *Nepeta cataria*[125], namely nepetalactone (XLV) and its analogues.

Together with completed investigations, studies have also been made where so far only the presence of attractants has been established in insects such as the moth of the tobacco hornworm [*Protoparce sexta* (Johannson)][126,127], the moth of the tobacco budworm [*Heliothis veriscens* (F.)][128], the moth of the lesser peach tree borer [*Synanthodon pictipes* (Grote and Robinson)][129], the beetles [*Rhopaea* (Ed. of Translation)] (Coleoptera: Scarabaeidae)[130], cockroaches (*Pycnoseelus suri* and *Nauphoeta cinerea*)[131,132], the apple fly (*Opius alloeus*)[133], the moth of the lesser apple worm[134], the moth of the sugarcane borer [*Diatraca saccharilis*

(F.)][135], the ambrosia beetle [*Trypodendron lineatum* (Oliv.)][136], the Angoumois grain moth *Sitotroga cerealella* (Oliv.)[137], the red cotton bug *Dysdercus cingulatus*[138], the California red scale *Aonidiella aurantii*[139], and the leaf roller *Argurotaenia velutinana*[140]. It is to be expected that further studies in the field of attractants will yield interesting and practically important results.

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The Mechanism of Alkaline Catalytic Polymerisation of Hydrocarbon Monomers

A.A.Korotkov (deceased) and S.P.Mitsengendler

In contrast to free-radical polymerisation, there is no single theory of anionic polymerisation which could explain all the observed phenomena, these being treated usually from different standpoints. In the present review an attempt is made at a critical analysis of the existing hypotheses in this field. The bibliography includes 90 references.

The polymerisation of vinyl and divinyl compounds under the influence of alkali metals and their organic compounds is regarded by the majority of investigators as successive organometallic synthesis[1-5]. As a result of repeated stepwise addition of monomer molecules to the initial organometallic compound, a polymer with a high molecular weight is formed. If a fresh portion of monomer is added to such a polymeric organometallic compound, the former adds to the macromolecule and polymerisation is restarted. Szwarc very aptly called such growing polymer chains "living" polymers[6].

The growth of a "living" polymer occurs of course in the absence of impurities from the reaction medium (water, alcohol, aldehydes) and in the absence from the monomer of functional groups which could interact with the organometallic compounds.

In 1928 Ziegler[1,2] concluded, on the basis of his own experimental data and those of Schlenk[7] and other investigators, that the polymerisation of butadiene under the influence of sodium is a complex consecutive reaction in which the monomer adds to the organic disodium compound at each stage:

$$2\,Na + CH_2{=}CH{-}CH{=}CH_2 \rightarrow NaCH_2{-}CH{=}CH{-}CH_2Na \quad \text{or} \quad NaCH_2{-}\underset{\displaystyle CH{=}CH_2}{\underset{|}{CHNa}},$$

$$NaCH_2{-}CH{=}CH{-}CH_2Na + CH_2{=}CH{-}CH{=}CH_2 \rightarrow$$

$$\rightarrow NaCH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2Na,$$

$$NaCH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2Na + CH_2{=}CH{-}CH{=}CH_2 \rightarrow,$$

$$\rightarrow NaCH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2Na,$$

etc.

If an organosodium compound is used instead of metallic sodium, the mechanism of the growth of the polymeric chains does not change, only the monomer now adds to the monosodium compound:

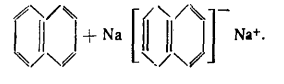
$$RNa + CH_2{=}CH{-}CH{=}CH_2 \rightarrow R{-}CH{-}CH{=}CH{-}CH_2Na\ .$$

Ziegler succeeded in isolating the intermediate products and in showing the stepwise occurrence of polymerisation. A characteristic feature of such stepwise reactions is the gradual growth of the molecular weight of the polymer with time. At low temperatures it is possible to terminate the chain growth at any stage. The degree of polymerisation is determined by the ratio of the amounts of monomer and catalyst consumed.

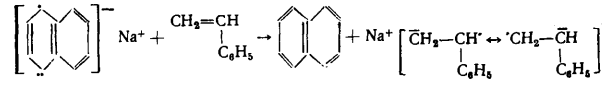
Ziegler[8,9], Medvedev[10], and Morton[11-13] pointed out the unusual form of the polymerisation reactions of vinyl monomers under the action of organic derivatives of alkali metals. For example, triphenylmethylsodium and diphenylethylpotassium polymerise butadiene and styrene with formation of polymers having relatively high molecular weights. Even in the presence of a large excess of the catalyst it is impossible to isolate the primary addition products of butadiene or styrene to the organometallic compound. When solutions of the monomer and the organometallic compound are mixed, the colour of the latter fades or disappears completely, but after the completion of polymerisation it is restored[10], i.e. the organometallic compound is hardly consumed and is regenerated. In contrast to the stepwise reactions, these processes were called catalytic. It was postulated that such catalytic polymerisation reactions must take place by a mechanism different from that of stepwise polymerisation. Contrary views were put forward on this subject: in his catalytic polymerisation Ziegler also isolated intermediate low-molecular products and thereby showed that the mechanism of the catalytic and stepwise polymerisation is the same[9].

Using an Alfin catalyst (typical) for catalytic polymerisation) and butyl-lithium (typical for stepwise polymerisation), Korotkov[14,15] obtained copolymers with the same composition. This confirmed that the reaction mechanism is the same in both cases. The observed differences in stepwise and catalytic polymerisation are related, according to Ziegler[9] and Korotkov[14], to the difference in the relative rates of initiation of polymerisation and of chain propagation and termination.

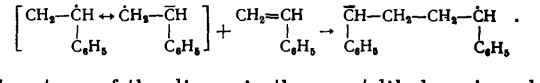
In recent years Szwarc and coworkers[3,16-18] put forward a new view concerning the mechanism of similar reactions. On dissolving in tetrahydrofuran in the presence of condensed aromatic compounds, metallic sodium forms a coloured complex[19,20]:



According to Szwarc, when a monomer is added to this compound, an electron is transferred from naphthalene-sodium to the monomer with formation of a radical-ion in which the unpaired electron is not localised, i.e. the compound formed is neither a true anion nor a true radical:

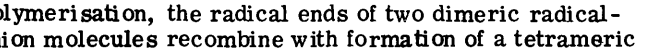


It was suggested that the radical-anion is formed only after the addition of a second styrene molecule without direct interaction between the three electrons:

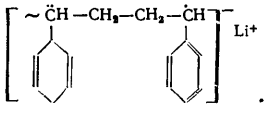


This structure of the dimer is the most likely, since both the anion and the radical are stabilised by the phenyl group. The dimeric radical-anion formed can, in principle, combine with styrene both by an anionic and a radical mechanism. As a rule, under the conditions of low-temperature

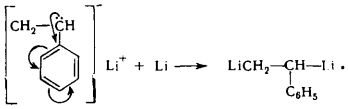
polymerisation, the radical ends of two dimeric radical-anion molecules recombine with formation of a tetrameric dianion, which becomes the sole active centre for polymerisation



Electron transfer from naphthalenesodium to the monomer takes place very rapidly in tetrahydrofuran but not at all in hydrocarbon media. Tobolsky's work [21-26] on the copolymerisation of styrene and methyl methacrylate in the presence of dispersed metallic lithium constitutes an experimental confirmation of Szwarc's hypothesis. The copolymers formed had in some cases an enchanced content of styrene units instead of being virtually pure poly(methyl methacrylate), which is obtained with other anionic catalysts, for example butyl-lithium. To account for the anomalous composition of the polymer, it was assumed that initiation with lithium is analogous to the reaction with naphthalenesodium, i.e. an electron is transferred from lithium to styrene with formation of a radical-anion with separated electrons:



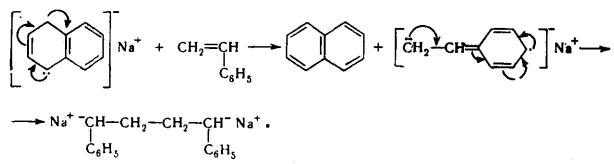
Such an active centre gives rise to further chain propagation by a radical mechanism at one end and by an anionic mechanism at the other. The enhanced styrene content in the resulting copolymer is due to polymerisation by a radical mechanism. In polar solvents the content of styrene units is sharply reduced. However, Korotkov and coworkers[27] obtained similar results in the polymerisation of styrene with methyl methacrylate in the presence of a typical anionic catalyst—solid methyl-lithium. It is suggested that the characteristic features of the reaction involving electron transfer from naphthalenesodium to styrene in solution should not apply to reactions with electron transfer from the surface of the metal, which occurs in the interaction of styrene with metallic lithium. Tobolsky's data are interpreted as follows: since, as a result of the primary initiation step, a radical-ion (styryllithium) is formed on the surface of the metal, its electron unsaturation must be immediately compensated by the electrons of the metal, which are highly mobile. As a result of the interaction between styrene and lithium, a dilithium compound should form:



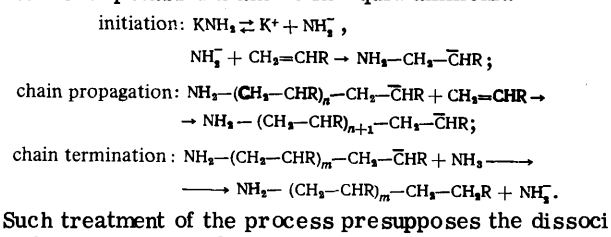
Because of the low solubility of the latter, chain propagation on the surface of the metal takes place preferentially with participation of the more readily adsorbed monomer. In this case styrene is evidently such a monomer.

After the polymeric chains reach a sufficiently large size and dissolve in the form of a dianion, the usual anionic polymerisation begins, in which virtually methyl methacrylate alone is incorporated in the polymeric chain. This leads to the formation of block polymers. On the other hand, in the copolymerisation of monomers with similar adsorption properties (for example, butadiene and styrene), the composition of the copolymer is independent of the heterogeneity of the catalyst or medium. Thus Tobolsky's results cannot serve as an unambiguous confirmation of Szwarc's hypothesis of the formation of a radical-anion with separated electrons.

On the basis of data on the copolymerisation of styrene and methyl methacrylate in the presence of anionic catalysts, Korotkov and coworkers[27] suggest that in polymerisation under homogeneous conditions the stage involving the formation of a radical-anion with separated electrons is absent. Dianions are formed by dimerisation in the initial initiation stage:

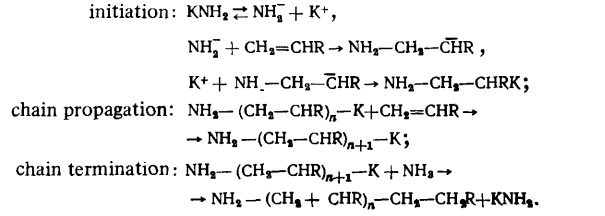


Price[28] was the first to suggest that alkaline polymerisation be regarded as an anionic process in which the active centre is trivalent negatively charged carbon (carbanion). Subsequently Sounderson and Hauser[29] and Higginson and Wooding[30] attempted to confirm experimentally the suggested mechanism. For example, the following mechanism was proposed for the polymerisation of styrene under the action of potassium amide in liquid ammonia[30]:



Such treatment of the process presupposes the dissociation of potassium amide into a free anion and cation. The attacking anion dissociates the double bond of the monomer with formation of a covalent bond at one end of the molecule and an active centre (carbanion) at the other. It is suggested that, within the limits of Coulombic attraction, the anion acts as an independent species, which is not bound to the counterion.

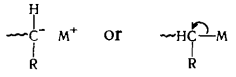
The mechanism quoted above was confirmed by kinetic studies on polymerisation carried out by Higginson, who showed that the rate of polymerisation is proportional to the concentration of the monomer and the amide ion, and that each polymer molecule contains the NH_2 group, while the molecular weight is independent of the concentration of the catalyst and is proportional to the concentration of the monomer. However, the results obtained can be explained with equal success on the basis of Ziegler's hypothesis by postulating the following mechanism for this reaction[31]:



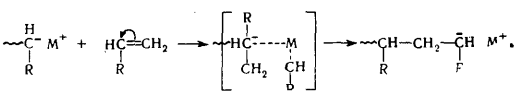
In this type of stepwise mechanism the equation for polymerisation kinetics and the dependence of the average molecular weight on the kinetic constants and the reactant concentrations are consistent with Higginson's relations obtained on the basis of an ionic mechanism of the reaction. Furthermore, Shatenshtein[32] showed that styrene polymerises on the surface of solid potassium amide, when the latter is not dissociated, and that this reaction cannot therefore be used as an unambiguous confirmation of Price's hypothesis.

Extensive experimental data confirm that the counterion always participates in the polymeric chain propagation steps. If the polymerisation centre were a free carbanion, the nature of the catalyst cation could affect only the rate of initiation of polymerisation centres but not the elementary chain propagation reaction. According to experimental data, the microstructure and properties of polymers, i.e. all the factors that are determined by the nature of the reaction, depend on the cation. For example, it is known that the content of 1,2- and 3,4-units in polydienes depends strongly on the nature of the cation[10,14,33,34] and that the stereoregularity of the polymer also depends on the latter[35,36]. Likewise the composition of the copolymers changes sharply on going from organolithium and organosodium compounds to organopotassium compounds[14,21,35,37]. The above differences in the structure of polymers and the composition of copolymers are sometimes explained by differences in the mechanism of the process. For example, it is believed that polymerisation in the presence of organolithium and organopotassium compounds takes place both by a radical and by an anionic mechanism, the relative contributions of which depend on the polymerisation conditions (the nature of the metal and medium)[5,34-42].

The experimental data on the effect of the catalyst metal on the rate and mode of polymerisation led the majority of investigators to the conclusion that in a hydrocarbon medium the active polymerisation centre is an ion pair or dipole[5,43-47]:



which is regenerated at the ends of the polymeric chains after the addition of each monomer molecule in the propagation step:



In polymerisation in the presence of catalysts which are readily ionised, for example, organosodium and organopotassium compounds in a strongly solvating or polar solvent, it is assumed that the degree of ionisation of the dipole is greatly enhanced and the active centre is regarded as a carbanion.

The hypotheses enumerated above have common features despite the apparent differences. The common features are that the polymerisation is regarded as a stepwise reaction involving consecutive addition of monomeric molecules to active centres, which may be anions or ion pairs, and therefore the nature of the active centres is analogous to that of the initial organometallic compounds.

Such treatment constitutes essentially a development of Ziegler's hypothesis with the sole difference that in the latter the C–M bond was regarded as covalent while in the new treatment it is regarded as ionic or of the ion–dipole type. A further difference is that, in the examination of actual reactions, account is now taken of the polarity of the bond in the terminal groups as a function of the structure of the monomer, the solvent, the nature of the metal, and other reaction conditions.

The experimental data which have accumulated in recent years cannot be accounted for from the standpoint of the stepwise polymerisation mechanism. To interpret the observed deviations, auxiliary hypotheses and assumptions are introduced. Some of the most typical cases are described below.

Thus regeneration of the catalyst after the completion of the polymerisation of butadiene or styrene in the presence of organic derivatives of alkali metals[8-10] (the reappearance of the initial colour of the solution) cannot be explained by regarding polymerisation as organometallic synthesis. For example, in the polymerisation of butadiene Ziegler[8,9] explained the reappearance of the colour of the initial catalyst (triphenylmethylsodium) by the metallation of traces of triphenylmethane. However, it is not clear why the metallation of the mobile hydrogen of triphenylmethane begins only after the completion of the polymerisation of butadiene. A similar case of regeneration of the catalyst in the polymerisation of butadiene in the presence of phenylisopropylpotassium in ethyl ether was accounted for by the possibility of the occurrence of a special case of "chain catalysis", but the mechanism of polymerisation and catalyst regeneration was not given[10].

In the polymerisation of isoprene[48], butadiene[49], and styrene[5,43] under the influence of butyl-lithium in a hydrocarbon medium and also of α-methylstyrene in the presence of naphthalenesodium in tetrahydrofuran[50] an anomalous variation of the reaction rate with the initial concentration of the organometallic compound was observed. The rate of reaction is independent of the initial concentration of the catalyst (n_0) when the latter is high and the resulting relation – $dm/dt = f(n_0)$ is represented by a curve exhibiting saturation.

This anomalous behaviour is explained by the specific properties of the organolithium compounds, namely the formation by the latter of association complexes in the hydrocarbon medium which are inactive in polymerisation[51-60]. For example, Welch[43] postulates the presence in the hydrocarbon medium of a dynamic equilibrium between the inactive associated molecules of the organolithium compounds and their monomeric active form:

$$(RLi)_n \overset{k}{\rightleftarrows} n\,RLi,$$

where R is butyl or polymeric radicals. In this case the rate of polymerisation reaction must be proportional to the sixth or seventh root of the initial concentration of butyllithium (for $n = 6$ or 7) and the variation of the rate of polymerisation of styrene with catalyst concentration will be represented by a curve exhibiting saturation. The hypothesis of the presence of association complexes combined with various assumptions makes it possible to explain for a number of cases the results of many investigations[53] and therefore it has found wide application and acceptance[5,52-64]. However, the proposed interpretation still requires a quantitative test. The adherents of the stepwise polymerisation mechanism, who assume that the nature of the active centres is the same as that of the initial organometallic compound, believe that the stability of the association complexes of the growing chains depends on the nature of the monomer, which explains the differences in the activity of monomers in polymerisation[68]. The higher activity of styrene compared with isoprene or butadiene when these are polymerised separately is attributed to the greater tendency of the growing polydiene chains towards association. However, the much lower activity of styrene compared with the above dienes in copolymerisation then becomes incomprehensible. Furthermore, it is known that the degree of association of organolithium compounds falls with increase in the size of the alkyl radical[46,65]. Therefore, on going from ethyllithium to polymeric lithium alkyls the anomaly in the dependence of the rate of polymerisation on the concentration of lithium alkyls should become less pronounced. However, this is not observed. For this reason, in the

formation of association complexes of mixed organolithium compounds (initial and high-molecular) the polymeric lithium alkyls should be present predominantly in the dissociated state. This must lead to the incomplete utilisation of the initial catalyst (for example butyl-lithium, even at relatively low concentrations of the latter), which should result in the formation of a polymer with a wide molecular weight distribution and a high number-average molecular weight. In anionic polymerisation the polymers obtained have as a rule a narrow molecular weight distribution and the degree of polymerisation is equal to the ratio of the concentrations of the monomer and the catalyst, i.e. all the initial organolithium compounds participate in the process. The evidence in favour of the presence of association complexes of "living" lithium polyalkyls, based on the observation that the viscosity of solutions of "living" polydienes falls on addition of butyl-lithium[66], tetrahydrofuran, or alcohol[67-69], cannot be regarded as unambiguous proof. The postulate that the anomalous relation $dm/dt = f(n_0)$ is due to the association of the organometallic compound in the hydrocarbon medium is inconsistent with the data of Podolsky and Korotkov[50] on the polymerisation of α-methylstyrene under the action of naphthylsodium in tetrahydrofuran. It was shown that in tetrahydrofuran, where organometallic compounds are not associated[43,57-67, 70,71], the rate of polymerisation is also independent of the initial concentrations of the catalyst when the latter are high. A similar anomalous relation was observed by Szwarc and coworkers and Schulz and coworkers[72-75] in the polymerisation of styrene in tetrahydrofuran under the influence of "living" polystyrene. They found that the polymerisation rate constant decreases with the initial concentration of the "living" polymer. The rate constant was calculated on the hypothesis that the reaction takes place without termination by a stepwise mechanism. Since it was assumed that the concentration of the active ends of the "living" polymer does not change during the reaction, the calculation was based on the equation for the kinetics of a pseudounimolecular reaction. To account for the anomalous relation, the authors put forward additional postulates, directly opposed to those discussed earlier, assuming that "living" polymers are dissociated in tetrahydrofuran:

$$\sim CH_2-\underset{\underset{C_6H_5}{|}}{CH}\sim Na^+ \rightleftharpoons \sim CH_2-\underset{\underset{C_6H_5}{|}}{\bar{C}H} + Na^+,$$

and that both the ion pair and the free carbanion behave as polymerisation centres but of course with different activities. This conclusion was based on the observed electrical conductivity of the "living" polystyrene in tetrahydrofuran[76] and also the finding that the addition of tetraphenylboronsodium led to a sharp reduction of the reaction rate constant, which depended little on the initial concentration of the "living" polystyrene[76-78]. The sharp decrease of the rate of polymerisation was regarded as evidence that at the ends of the growing chains there are free anions, whose concentration falls very appreciably on introduction of tetraphenylboronsodium, due to a sharp increase of the concentration of the counterions as a result of the dissociation reaction

$$[(C_6H_5)_4B]Na \rightleftarrows [(C_6H_5)_4B]^- + Na^+.$$

Fundamentally new hypotheses concerning the mechanism of homogeneous catalytic polymerisation in the presence of organometallic compounds were put forward by Korotkov[48,50,79-84]. On the basis of an analysis of the polymerisation kinetics and also by studying the dependence of the average molecular weight of the polymer and its molecular weight distribution on the concentrations of the initial reactants and the rate constants of the elementary reactions, he justified the hypothesis that anionic polymerisation is of a coordination type and that it takes place in a much more complex manner than would appear on the basis of the stepwise mechanism. In the suggested hypothesis the active polymerisation centres are regarded not as organometallic compounds but as more reactive complexes of the monomer and the organometallic compounds, formed using the π-electrons of the unsaturated compound and the p-electrons of the valence shell of the metal:

$$RNa + \underset{\underset{CHR}{\|}}{CH_2} \overset{k_1}{\rightleftarrows} R{:}Na{:}\ \underset{\underset{CHR}{|}}{CH_2}. \qquad (1)$$

In such complex compounds with a coordination number of two the disposition of ligands relative to the central atom (the metal) must be close to linearity, which ensures their relative stability. On the other hand, owing to the weakening and the polarisation of the C–M bond and also the coordination unsaturation of the central atom (alkali metal), the reactivity of these compounds increases and the addition of a second monomer molecule (chain propagation) should take place at a much higher rate:

$$\underset{\underset{CH_2}{\|}}{CHR} + R{:}\,Na{:}\ \underset{\underset{CH_2}{|}}{CHR} \xrightarrow{k_2'} RHC-CH_2 \xrightarrow{k_2'''} R-CH_2-CHR-Na{:}CH_2-CHR. \qquad (2)$$
$$\underset{\underset{CH_2}{|}}{CHR} \xleftarrow{k_2''} R{:}\,\ddot{N}a{:}CHR$$
$$\qquad\qquad\qquad

the addition of the first monomer molecule [Eqn. (2)] and the second, the catalytic coordination reaction, in which the initial organometallic compound retains its individuality in the propagation stage, i.e. participates in its entirety in the construction of the polymerisation active centre[81]:

$$RNa + M \xrightarrow{k_3} RNaM^*, \qquad (5)$$

$$RNaM_i^* \xrightarrow{k_3} RNaM_{i+1}^*,$$

but loses its individuality in the termination stage† [see mechanism(3)].

The organometallic compounds formed by reaction (3) (a, b, c) are capable of again initiating polymerisation, but now by the stepwise coordination mechanism.

On the basis of these postulates, Korotkov derived an equation for the kinetics of non-steady-state reactions and the degree of polymerisation using a new variable φ, which is called the effective time and which is related to the true time by the expression $d\varphi = mdt$, i.e. $\varphi = \int_0^t \bar{m}dt$, where m is the concentration of the monomer and t the reaction time.

The relations obtained explain the observed phenomena in the region of catalytic polymerisation. Thus it was shown that the complex relation between the rate of polymerisation and catalyst concentration described above, which is represented by a curve exhibiting saturation, is associated with the occurrence of kinetic chain termination [reaction (3)] and the complex form of the $x-\varphi$ kinetic curves is due to the nature of the termination [reaction (3) (a, b, c)]. While direct proportionality between the extent of polymerisation and x and φ is characteristic of the stepwise mechanism, i.e. $x = f(\varphi)$, in the coordination mechanism at a high degree of conversion the kinetic curves as a rule "bend" to the right in the presence of termination, in accordance with mechanisms (3a) and (3b) and to the left in termination by mechanism (3c). Since the propagation of the polymeric chain alternates with "rest periods" (kinetic termination), such a mechanism should result, in contrast to the stepwise mechanism, in the formation of polymers with a fairly narrow molecular weight distribution, approaching the Gaussian distribution, with a slow fall-off at high molecular weights. It has been shown for the polymerisation of φ-methylstyrene under the action of naphthylsodium in tetrahydrofuran at −78 °C as an example[50] that the experimental data for the kinetics $[x = F(t, \varphi)]$, the number-average molecular weight $[\bar{M} = F(n_0)]$, and the molecular weight distribution are in good agreement with the results calculated on the hypothesis that the polymerisation takes place consecutively by the catalytic coordination and stepwise coordination mechanisms. It is suggested[83] that the decrease of the polymerisation rate constants with increasing catalyst concentration observed by Szwarc and coworkers[77, 78] is not due to the fact that the polymerisation centres are both free ions and ion pairs but is caused by the kinetic termination of the growing chain, which becomes more pronounced in the presence of $[(C_6H_5)_4B]Na$.

According to the coordination mechanism, the effect of electron-donor additives (tetrahydrofuran, ethyl ether, amines) on the rate of polymerisation, the polymer structure, and also the composition of the copolymers[14,50,81-84] is not attributed to the dissociation of the organilithium compounds but to the capacity of these additives to form fairly stable complexes with the organometallic compounds, for example:

$$R^1:Li + 2(C_2H_5)_2O \rightleftharpoons R^1:Li\begin{matrix}:O(C_2H_5)_2\\:O(C_2H_5)_2\end{matrix}.$$

Esters and amines are more powerful bases than any unsaturated hydrocarbon capable of polymerisation. Therefore the formation of intermediate lithium (or sodium) complexes with a higher coordination number is postulated in the presence of such bases[82,84,85]:

$$R^1:Li\begin{matrix}:O(C_2H_5)_2\\:O(C_2H_5)_2\end{matrix} \rightleftharpoons R^1:Li\begin{matrix}:O(C_2H_5)_2\\:O(C_2H_5)_2\\H_2C{=}CHR\end{matrix}.$$

Nor can one exclude the possibility of the formation of mixed complexes resulting from the displacement of an ether molecule by the monomer:

$$R^1:Li\begin{matrix}:O(C_2H_5)_2\\:O(C_2H_5)_2\end{matrix} + \begin{matrix}CH_2\\\|\\CHR\end{matrix} \longrightarrow R^1:Li\begin{matrix}:O(C_2H_5)_2\\:CH_2\\CHR\end{matrix} + (C_2H_5)_2O.$$

In such compounds the R′–Li bond is more strongly polarised than in complex hydrocarbon compounds and the group R′ is more reactive. This is responsible for the low stability of the compound as a whole and therefore also for the higher rate of intramolecular isomerisation. We believe that all these factors are decisive in the acceleration of polymerisation according to the mechanism

$$\sim CH_2{-}\underset{R}{CH}:Li\begin{matrix}:O(C_2H_5)_2\\:O(C_2H_5)_2\end{matrix} + \begin{matrix}CH_2\\\|\\CHR\end{matrix} \longrightarrow \sim CH_2{-}\underset{R}{\overset{H_2C{-}CHR}{CH}}:Li\begin{matrix}:O(C_2H_5)_2\\:O(C_2H_5)_2\end{matrix} \longrightarrow$$

$$\longrightarrow \sim CH_2{-}\underset{R}{CH}{-}CH_2{-}\underset{R}{CH}:Li\begin{matrix}:O(C_2H_5)_2\\:O(C_2H_5)_2\end{matrix}.$$

The hypothesis that elementary reactions, in particular the chain propagation reaction, take place via relatively stable intermediate complexes, explains satisfactorily the observed change in the activity of two monomers on transition from separate polymerisation to copolymerisation[82,86-90]. For example, styrene, which is more reactive than butadiene in separate polymerisation, becomes relatively inactive in the copolymerisation of these monomers[87]. This is because butadiene forms relatively more stable intermediate complexes than styrene and the composition of these complexes in fact determines the composition of the copolymer. On the other hand, the isomerisation of the intermediate complex to an active centre affects only the overall rate but not the composition of the copolymer. In copolymerisation in a hydrocarbon medium butadiene is 400 times more reactive than styrene. In a strongly solvating medium, for example in tetrahydrofuran, the capacity for the formation of the butadiene complex decreases and its reactivity falls relative to styrene[84].

It follows from the above that in the field of catalytic "anionic" polymerisation of vinyl and diene monomers in the presence of organometallic compounds, two main hypotheses concerning the nature of the active centres exist so far. In one of these the active centres are regarded as ion pairs capable of dissociation in the limit into ions and it is supposed that the process takes place by a stepwise mechanism, i.e. via two elementary reactions. In the second hypothesis polymerisation is regarded as a coordination process proceeding via intermediate complexes of the monomers with the initial organometallic compounds. The polymerisation then consists of not less than three elementary reactions.

†The regeneration of the catalyst after the completion of polymerisation observed in the experiments of Ziegler, Medvedev, and Morton described above (see Russ. p. 277), can be explained from the standpoint of this hypothesis by a reaction according to the catalytic coordination mechanism.

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Institute of Macromolecular Compounds,
USSR Academy of Sciences, Leningrad

U.D.C. 620.193.91

The Mechanism of Light-induced Ageing and Light Stabilisation of Polymers

Yu.A.Ershov, S.I.Kuzina, and M.B.Neiman (deceased)

This review deals with processes accompanying the light-induced ageing of polymers which are subjected simultaneously to the action of oxygen and ultraviolet and visible light, and also with the distinctive features of these processes and possible pathways for the stabilisation of polymeric materials. Under natural conditions, solar radiation leads to rapid mechanical breakdown of unstabilised polymeric materials. The light stabilisation of polymers is one of the most important problems, because of the wide application of these materials[1] in space engineering, national economy, and ordinary life.
The authors' aim was not to give the maximum cover of the available literature on this problem, which has become fairly extensive during the last 5–6 years; attention is mainly concentrated on the mechanisms of the processes occurring in light-induced ageing and the methods available for their investigation. The bibliography includes 122 references.

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1. CHANGE IN THE PRACTICAL PROPERTIES OF POLYMERS ON LIGHT-INDUCED AGEING

In most studies of light-induced ageing, the mechanical properties of polymers have been investigated as a function of the duration and conditions of irradiation[2-6]. This is quite reasonable, since the user is interested in the first place in the stability of such properties of the material as elasticity, strength, adhesion, constancy of dimensions, etc. However, most of the published work is of an unduly applied nature and reduces to simple statements of the magnitude of the changes occurring and the effect on these changes of various stabilisers against light.

Mechanical methods for testing polymers are most widely used. They are readily available and are highly sensitive. The changes in the ultimate strength and the relative elongation of polymer specimens as a function of the duration of irradiation are most frequently determined. The user obtains in this way virtually exhaustive data on the operational properties of the material, but, for a controlled increase of the stability of polymers with respect to light, it is necessary to know the internal mechanism of the observed changes.

Quantitative theory[7-9] relating the mechanical characteristics of the polymeric material to the chemical structure and the nature of the supermolecular structures is still in its development stage. A clear relation between the following changes in polymeric materials on light-induced ageing is by no means always clear: changes in chemical structure as a result of photochemical reactions, changes in supermolecular and hence crystalline structures as a result of the changes in chemical structure, and the changes in mechanical properties resulting from the changes in crystal structure. It is quite evident that, in studying the action of light on mechanical properties, it is necessary to follow the entire sequence of transformations. Only then can one hope to establish a quantitative relation between the first and last stages of the light-induced ageing process.

Instructive studies have been made by Baltenas[10,11] and by Ozawa and coworkers[5]. A number of polyethylene specimens differing in the number of local strains in the defects were investigated[10]: (1) a film (60μm) heat-treated in a vacuum above the melting point (this film is closest to equilibrium); (2) a film (60 μm) extruded under conditions of hot orientation and rapid cooling with high anisotropy of the mechanical properties, an irregular spherulitic structure, and local internal strains; (3) specimens obtained by cold drawing (neck) with breakdown into fibrils of the spherulitic structure and the maximum number of local strains. The specimens were irradiated with ultraviolet light from a PRK-2 lamp at 40°C in air over a period of 20 h.[13] On going from specimens (1) with a homogeneous spherulitic structure to specimens (2) and (3) with an increasingly defective structure, one observes an increase in the rate of accumulation of carbonyl groups (determined from infrared spectra), a more rapid decrease of mechanical strength, and an increase in the yellow colour of the specimens. These observations are consistent with the hypothesis[14] that the strength of the chemical bonds decreases with increasing mechanical strain in the specimen.

The study of the thermograms of the same specimens shows that, on light-induced ageing, the degree of crystallinity increases in all cases by 6–8%. Hence one may conclude that chemical bonds in the region of local strains are the first to dissociate in light-induced ageing, which may lead to the migration of units from the region of the defects to the crystal lattice. The so called destructive crystallisation takes place. The increase in the degree of crystallinity on ageing was noted also by other workers[5,15,16]. Thus the change in the properties of the polymeric material in light-induced ageing is determined mainly by the nature of the defects and not the structure of the crystal lattice[10].

The data quoted by Baltenas and Visciniene[12] are very instructive in this respect. The structure of the polyethylene coating of an aluminium foil is determined to a large extent by the method of its preparation. Fig. 1

presents the photomicrographs of sections of polyethylene coatings obtained by centrifugal deposition in a fluidised layer of polyethylene powder at 200°C. Slow cooling of the coating obtained in air results in a structure with large annular spherulites (Fig. 1*a*). On rapid cooling with water, smaller spherulites without visible rings are produced (Fig. 1*b*). Furthermore, in the latter case amorphous regions arise, particularly at the surface of the coating, without a visible spherulitic structure. It is found that the coating with a crystalline surface is more stable with respect to the action of ultraviolet light. Fig. 2 presents photomicrographs of the surface of the coating after irradiation for 30 h. On the coating with the crystalline surface (Fig. 2*a*), there are almost no cracks, while the coating with the amorphous surface (Fig. 2*b*) was virtually broken up as a result of the formation of a large number of cracks.

Figure 1. Spherulitic structure of a polyethylene coating in transverse section: *a*) obtained by centrifugal deposition with cooling in air; *b*) ditto with cooling in water.

The difference in the structures of the polymer is in turn determined by the chemical reactions occurring in the preparation of the coating. The formation of the structure with large spherulites on centrifugal deposition is probably caused by the thermal oxidation of polyethylene. In thermal oxidation in the melt, the macromolecules dissociate with formation of free radicals, whose reactions lead to the formation of oxygen-containing groups and to the cross-linking of the chains. It is suggested[17] that these chemical reactions appreciably alter the conditions for the formation of crystallisation nuclei (nucleation), as a result of which, the rate of their formation falls. There is a change in the relative rates of nucleation and crystallisation, which leads to the formation of large spherulites. The generation of amorphous regions on rapid cooling is due to the sharp decrease of the rate of nucleation. In the unoxidised polyethylene amorphous regions of this kind are absent. The increase of the rate of the light-induced ageing of the coating in the presence of amorphous regions may be caused by its higher permeability to oxygen.

The dependence of stability with respect to light on the dimensions of the crystalline regions and the degree of orientation of low-pressure polyethylene films has been investigated with irradiation, using a weatherometer, with light at a wavelength of 360–420 nm.[5]

The size of the crystallites and the molecular weight change little on irradiation. It is interesting to note that refusion of the specimens fully restores their mechanical properties. The authors' explanation is that amorphous regions of the polymel are the first to undergo polychemical oxidation, after which new crystalline regions appear, while large crystals break down under the action of high-energy quanta, giving rise to internal strains with weakened chemical bonds.

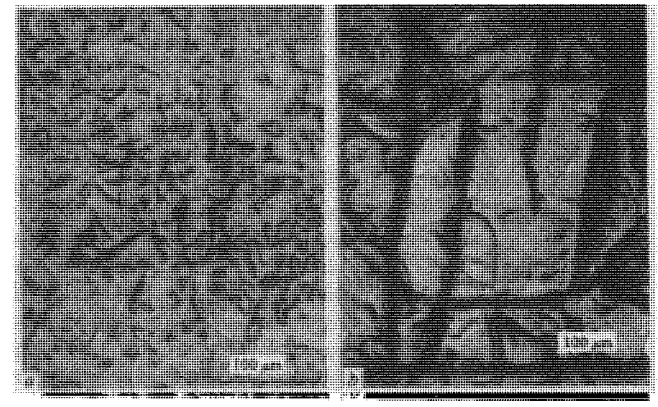


Figure 2. Photomicrographs of the surface of a polyethylene coating (viewed from above) after irradiation for 30 h with ultraviolet light: *a*) cooling in air; *b*) cooling with water.

The results obtained in the oxidation of polymers with different extents of branching provide an indirect indication of the relation between the light stability of the polymer and the structure of its macromolecules[18]. On irradiation with ultraviolet light (280 nm), polyolefins absorb oxygen at different rates depending on the degree of branching (Fig. 3).

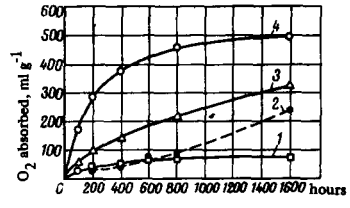


Figure 3. Variation of the extent of absorption of oxygen with the degree of branching of polyolefin specimens irradiated with ultraviolet light at a wavelength of 280 nm at 50°C: 1) linear polyethylene; 2) branched-polyethylene; 3) isotactic polypropylene; 4) poly-4-methylpent-1-ene.

Thus it is clear from the studies enumerated above that, although chemical reactions are important, they are by no means the sole factor determining the mechanical strength on light-induced ageing of polymeric materials and it is particularly important to take this into account in thermal processing of polymers.

The relation between the mechanical properties and chemical transformations in light-induced ageing of polymers has been investigated in greatest detail for the formation of cross-links on ultraviolet irradiation. The large number of studies on this problem has been stimulated by the cross-linking theory developed in detail for the ageing of polymers under the action of ionising radiation[19,20]. Although structure formation takes place under these conditions too, chemical reactions play a decisive role in this case, which makes it possible to establish certain quantitative relations between the number of cross-links and the mechanical properties.

2. KINETIC MECHANISM OF THE PHOTOCHEMICAL PROCESSES IN LIGHT-INDUCED AGEING

From the standpoint of the kinetics, the process of light-induced ageing of polymers can be divided into a number of stages, each of which is characterised by its own rate constant. These stages can occur both consecutively and simultaneously. In the latter case a number of competing reactions are observed, one of which may predominate, depending on the conditions.

Among the large number of studies dealing with the light-induced ageing of various polymers, there are only a few on the kinetic analysis of the results on the basis of a system of kinetic equations. This is fairly remarkable, because the studies on light-induced ageing are essentially kinetic, since the changes in a particular quantity are always investigated as a function of the duration of irradiation. The absence of kinetic analysis is due to the difficulties associated with the derivation and solution of an adequate system of kinetic equations and also with the complexity of the analysis of small amounts of products.

In this review an attempt is made to derive such a system and the solutions are analysed as far as possible.

1. Initation:

$$S + h\nu \xrightarrow{k_1} S^*, \qquad (1)$$

where S is a macromolecule containing an absorbing group in the ground singlet state and S^* the same macromolecule with the absorbing group in an excited singlet state.

2. Return to the initial state by light emission (fluorescence):

$$S^* \xrightarrow{k_2} S + h\nu'. \qquad (2)$$

3. Transition to an excited triplet state and a radiationless transition unaccompanied by dissociation:

$$S^* \xrightarrow{k_3} T; \quad S^* \xrightarrow{k_4} \tilde{S}, \qquad (3)$$

where $\tilde{S}$ is a molecule with excited vibrational states.

4. Return to the initial state by a singlet–singlet energy transfer (quenching of fluorescence):

$$S^* + A \xrightarrow{k_5} S + A^*, \qquad (4)$$

where A is an acceptor molecule.

5. Transformation of the triplet state:

$$T \xrightarrow{k_6}. \qquad (5)$$

6. Photodissociation:

$$S^* \xrightarrow{k_7} 2R. \qquad (6)$$

7. Formation of photolytic products:

$$M{-}M + R \xrightarrow{k_8} R + P_l, \qquad (7)$$

where M–M is a section of the macromolecule without an absorbing centre.

8. Cross-linking (chain termination) and diffusion of microradicals from the polymer matrix (linear termination):

$$2R \xrightarrow{k_9} C: \ R \ \text{(condensed phase)} \xrightarrow{k_9'} R \ \text{(gas)}. \qquad (8)$$

9. Oxidative processes:

$$R + O_2 \xrightarrow{k_{10}} P_0 + R, \qquad (9)$$

where P_0 are products obtained via a peroxy-radical; k_1–k_9 are the rate constants for the processes, ν is the frequency of the active light, and ν' the frequency of the light emitted in fluorescence (in the general case $\nu \neq \nu'$). The reversal of stage (4) results in sensitisation via impurities.

Despite the large number of stages quoted above, the mechanism is to a large extent simplified—in particular it is assumed that light-induced ageing takes place mainly via singlet states, the complex stages (7) and (9) are described by overall constants, quenching by oxygen is not taken into account, and it is assumed that various radicals have the same reactivity (the one-centre approximation). Stages (1)–(8) determine the kinetics of light-induced ageing in the absence of oxygen, i.e. in photolysis. The entire set of stages (1)–(9) describes oxidative ageing. Since all the photolytic processes can take place in oxidative light-induced ageing, the large number of studies dealing with the photolysis of various polymers is not surprising. The determination of the kinetic parameters for the photolytic breakdown of polymers is simpler than for oxidative ageing and yields important information about the initiation of photochemical processes. Usually[21–24] the first four stages of the mechanism, describing the physical photoactivation and deactivation processes, are not treated in detail and are combined in a single initiation stage. For example, the initiation stage in the photochemical oxidation of polyethylene[21,25] and polystyrene[26] is described as follows:

$$\ldots CH_2{-}CH_2{-}CH_2{-}CH_2\ldots \xrightarrow{h\nu,\ O_2} \ldots CH_2{-}CH_2{-}\underset{\displaystyle OOH}{CH}{-}CH_2\ldots,$$

$$\ldots CH_2{-}\underset{\displaystyle C_6H_5}{CH}{-}CH_2\ldots \xrightarrow{h\nu\ O_2} \ldots CH_2{-}\overset{\displaystyle OOH}{\underset{\displaystyle C_6H_5}{C}}{-}CH_2\ldots.$$

Undoubtedly mechanisms of this kind make it very difficult to understand the most important stage in light-induced ageing, namely initiation, and in photolysis by sunlight (λ = 290 nm) the nature of the light-absorption centres is completely obscure, since pure saturated hydrocarbons, for example, are transparent in this wavelength range.

3. THE MECHANISM OF INITIATION IN LIGHT-INDUCED AGEING. EXCITED STATES

The principal difference between photochemical and dark reactions is due to the nature of initiation of the process as a whole. In a dark reaction the energy required to overcome the activation barrier is drawn from the internal energy of the system and the rate and mechanism of the process under these conditions are determined by the temperature of the system. In a photochemical reaction the energy is provided from outside in the form of quanta of electromagnetic radiation and at a given temperature of the system the rate and mechanism of the process are determined by the intensity of the initiating radiation and its spectral distribution.

Usually[27,28] the primary photochemical step is regarded as the chemical reaction of the molecule excited by light absorption with formation of one or several primary photochemical products. However, the light absorption itself is essentially a chemical reaction of the molecule.

Indeed the chemical properties of the molecule are determined by the structure of its electron shell, which changes considerably on absorption of light; the chemical properties of the excited molecule, in particular its reactivity, may differ sharply from those of the molecule in the normal state[29,30].

Evidently, for a theoretical prediction of the nature of the excitation of the polymer molecule and hence of the entire light-induced ageing process as a function of the intensity of the incident radiation and its spectral distribution, it is necessary to have a clear idea about the nature of the absorbing groups and their electronic states.

The principal component of solar radiation at sea level consists of the long-wavelength region above 300 mn and only a small part of it is radiation at a wavelength less than 300 nm. The absorption spectra of the commonest polymers—poly(vinyl chloride) poly(methyl methacrylate), polystyrene, polyethylene, polypropylene, cellulose, polyamides, etc. —do not contain absorption bands in the region above 300 nm and therefore it would appear they should not undergo light-induced ageing. However, these polymers break down rapidly in sunlight. Hence it follows that it is precisely the small component of the short-wavelength solar radiation in the region of 300 nm that initiates the secondary photochemical processes leading to the light-induced ageing of polymers. The wings of the absorption bands attributed to carbonyl groups and polyene conjugated structures enter this region (the long-wavelength band of acetone is in the region of $\lambda_{max} = 280$ nm [31] and the band of $CH_3-(CH=CH)_4-CH_3$ is in the region of $\lambda_{max} = 290$ nm [32]). These groups and structures may be regarded as initiation centres for light-induced ageing in polymers whose monomer units do not contain absorbing groups†. The carbonyl group may form part of a monomer unit of the polymer, for example in polyamides, polymethacrylates, etc. In carbon chain polymers such as polyethylene, polypropylene, and polystyrene carbonyl groups and double bonds arise by thermal oxidation in the polymerisation and processing of the polymers.

An indirect demonstration of the role of C=O groups in light-induced ageing processes of polymers is provided by data on the photochemical degradation of poly(vinyl chloride) (with light at 300 nm). The photochemical degradation was appreciably accelerated on addition of acetone to the polymer[33,34].

The apparent absence of the corresponding bands in the absorption spectra of the polymers is due to the low concentration of the initiating groups and frequently the fact that such bands are masked by the intense bands associated with the chemical groups forming part of the monomer units of the polymer. For example, the spectrum of polystyrene is determined mainly by the absorption of the phenyl rings. Because of the difficulties of the direct spectroscopic determination of the absorbing groups of the above type, investigators resort to indirect methods (for example the measurement of the activation spectrum—the dependence of the quantum yields of the photochemical processes on the wavelength of the initiating radiation[35,36]) (Fig. 4).

It was also shown[37] that the maximum luminescence of polypropylene is observed on excitation with light at 280 nm, although in this region there is no detectable absorption maximum. Since the luminescence intensity is approximately proportional to the number of excited molecules, one may propose that, on irradiation with light at this wavelength, the most intense breakdown of the polymer will occur.

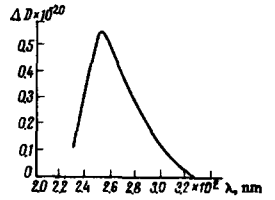


Figure 4. Variation of the optical density of poly(vinyl chloride) with the wavelength of ultraviolet radiation per incident quantum.

In view of the special role of carbonyl groups in light-induced ageing of various polymers, we shall consider in greater detail (as a model) the electronic structure of complex carbonyl-containing molecules[30,38]. It must be noted that the ultraviolet spectra and hence also the electronic structure of the carbonyl compounds of the polymers have been scarcely investigated and therefore the data quoted are suitable only for an approximate prediction of the course of photochemical processes in polymers.

The electronic structure of the carbonyl-containing compound in the region of the C=O group is determined by the presence of three groups of electrons:

(1) The non-bonding n electrons in the valence shell of the oxygen atom which do not enter into a chemical bond; (2) the bonding π electrons, the wave function of which is antisymmetric relative to the plane passing through the C=O bond; (3) the bonding σ electrons, the wave function of which is symmetrical relative to the axis of the C=O bond. The π electrons are usually delocalised in the region of the C=O group and the σ electrons are localised at the atoms which they bind together.

In a one-electron scheme these three groups of electrons correspond to three groups of levels (Fig. 5). The ground state of the molecule corresponds to the population of the one-electron states which ensures the minimum total energy of the molecule.

An excited state of the molecule arises as a result of the transition of one of the n, π, or σ electrons to an antibonding π^* or σ^* level. Depending on the nature of the transition, the excited states are denoted as follows: an $S_{n\pi^*}$ (singlet $n\pi^*$) state of the molecule arising by transition of a $2p$ electron from the n orbital to an antibonding π^* orbital, a $T_{n\pi^*}$ (triplet $n\pi^*$) state—a similar transition but with a change in the resultant spin of the system, etc.

The electronic absorption bands attributed to the carbonyl group are due to the corresponding transitions. The short-wavelength band with $\lambda_{max} = 150$ nm (8.3 eV) is due to the $\pi \rightarrow \pi^*$ transition, the middle band with $\lambda_{max} = 190$ nm (6.5 eV) corresponds to the $n \rightarrow \sigma^*$ transition, and the long-wavelength band with $\lambda_{max} = 280$ nm (4.4 eV), which is the most interesting from the standpoint of light-induced ageing, is caused by the $n \rightarrow \pi^*$ transition. In the region of the long-wavelength boundary of this band at

†The initiation can of course take place also via impurity molecules.

340 nm (3.6 eV) a vibrational structure is observed. In this transition both $S_{n\pi^*}$ and $T_{n\pi^*}$ excited states may be populated. Precisely these are the initial states in photochemical reactions undergone by various polymers with a carbonyl group in light-induced ageing and the concentration of these states must appear in the kinetic equations describing the light-induced ageing of a particular polymer.

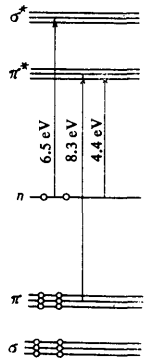


Figure 5. Schematic representation of one-electron levels in a molecule containing a carbonyl group.

Since under the usual experimental conditions absorption in the region of about 300 nm plays the main role, in the treatment below S^* must be understood as the $S_{n\pi^*}$ state. Eqns. (2)–(6) of the kinetic mechanism of light-induced ageing describe the processes involved in the degradation of the electronic excitation energy absorbed in the primary step (1). The relation between the rates of these processes ultimately determines the rate of light-induced ageing. Thus, for example, the number of breaks in the macromolecular chain (degradation), which has a destructive effect on the mechanical properties of the polymer, is determined (see below) by the relation $D = k_6 \int_0^t (S^*)dt = k_6(\bar{S}^*)t$, where $(\bar{S}^*)$ is the average concentration of excited states during the time of exposure t, i.e. with increasing (S^*), the rate of degradation of the polymer rises. However, if the rates of processes (2)–(5) are high, the concentration of excited states and hence also the rate of degradation are insignificant. The data for the constants k_2–k_5 may be obtained by spectroscopic luminescence techniques.

Many polymers in the solid state and in solution exhibit bright luminescence. Polymers with a wide variety of chemical structures, including biopolymers, have been investigated qualitatively[39]. The luminescence spectra‡ of all the polymers investigated extend as a continuum over the region 300–700 nm (when an ISP-51 glass spectrograph is used). This luminescence is not characteristic. It consists of maxima with fixed positions in the red part of the spectrum and the adjacent broad diffuse maximum in the blue-violet part. The latter maximum changes its position from compound to compound and with molecular weight in the same homologous series.

‡The observed glow has been referred to as fluorescence[39] without the appropriate evidence being adduced (see below).

Gachkovskii[39] did not explain the changes in the luminescence spectrum and their origin. It may be supposed that the observed glow is caused by the presence in the polymer of impurity groups, for example terminal groups, which consist of part of the initiator molecule. The relative content of these groups and therefore also the luminescence yield must fall with increasing molecular weight.

A more careful study of the luminescence of various polymers was carried out by Charlesby and Partridge[40,41]. The main aim of these investigations was to establish the nature of the centres responsible for the thermoluminescence observed when raising the temperature of the polymer specimens subjected to the action of γ-radiation or ultraviolet light at 77°K; the luminescence of the same polymers at room temperature, excited by ultraviolet light of different wavelengths, was studied simultaneously. The luminescence spectra of polyethylene, polypropylene, polystyrene, and polytetrafluoroethylene are produced by the superposition of the fluorescence spectra in the region of 300–400 nm and phosphorescence spectra in the region of 400–600 nm. The thermoluminescence spectra of these polymers are in the main analogous to their luminescence spectra.

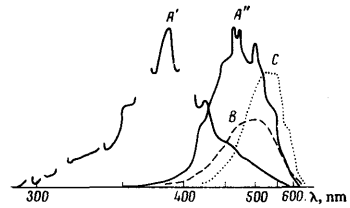


Figure 6. Luminescence spectrum of polyethylene: *A'*) and *A''*) complete luminescence spectrum; *B*) phosphorescence spectrum obtained on irradiation of polyethylene through a glass filter; *C*) phosphorescence spectrum obtained on irradiation of polyethylene through a filter transmitting light at wavelengths greater than 350 nm; the spectra are presented with different intensity scales.

Fig. 6 shows the luminescence spectrum of polyethylene resolved into the ultraviolet (*A'*) and visible (*A''*) components. The luminescence spectra of low- and high-density polyethylene are produced by the superposition of at least four spectra, which differ in structure and the limiting excitation wavelength. The complete phosphorescence spectrum (*A''*) of polyethylene consists of a series of sharp vibrational peaks against the background of a broad spectral band. Spectrum *B* is obtained when a glass filter, transmitting light at wavelengths greater than 300 nm, is interposed in the path of the exciting beam. Spectrum *C* is obtained with a filter transmitting light at a wavelength greater than 350 nm. The difference between spectrum *A''* and the sum of spectra *B* and *C* may be due to the presence of an undetected spectrum *D*. At a wavelength greater than 420 nm phosphorescence is not excited.

The phosphorescence spectrum of polystyrene is very similar to those of acetophenone and benzophenone, investigated by Kasha[42]. Kasha attributes the phosphorescence of benzophenone and acetophenone to the $n \rightarrow \pi^*$ transition of the carbonyl group. The distance between the distinct bands in the vibrational structure corresponding to the

stretching vibrations of the carbonyl group is 1665 cm^{-1} for benzophenone and 1690 cm^{-1} for acetophenone. In the phosphorescence spectrum of polystyrene this interval is 1600 ± 150 cm^{-1}. The great similarity of the phosphorescence spectrum of polystyrene to those of benzophenone and acetophenone can be hardly attributed to isolated admixtures of the latter. It is most likely that the phosphorescence of polystyrene is due to the presence of small amounts of carbonyl groups produced in the polymer during its preparation. Three types of carbonyl groups, two terminal and one distributed at random, are possible:

$$\underset{\underset{C_6H_5}{|}}{R-C=O}\ (I), \qquad \underset{\underset{H}{|}}{R-C=O}\ (II), \qquad \underset{\underset{O}{\|}}{R-C-R}\ (III).$$

The presence of these groups may explain the observed features of the phosphorescence spectra. Groups of type (I) give rise to a spectrum analogous to that of acetophenone but displaced towards the red region due to the presence of a heavy alkyl substituent—the polystyrene chain, as is observed for alkyl-substituted methyl ketones[43]. Spectra of groups (II) and (III) should be similar to those of aliphatic aldehydes and ketones and also polyethylene if the phosphorescence spectrum of the latter is due to carbonyl groups. These hypotheses are confirmed by experimental data. In particular, the fluorescence spectrum of polystyrene may be attributed to emission by carbonyl groups.

It is quite evident that the luminescence of polystyrene is not associated with the phosphorescence and fluorescence spectra of toluene (which should be the case if the isolated phenyl groups of the macrochain were responsible for the major part of the emission), since the 0,0 bands of toluene are in the region of 270 and 347 nm.[44] Nor can they be attributed to terminal groups, since the polystyrene was obtained by thermal polymerisation.

The luminescence of polyethylene cannot be due to the properties of the polyethylene chains, since saturated hydrocarbons do not luminesce. In this connection it is interesting to note that the entire luminescence spectrum is observed even in comparatively pure saturated hydrocarbons, such as, for example, pentatriacontane deposited in a thin layer on a quartz support.

It may be supposed that the luminescence of polyethylene is caused by the presence of double bonds in the chain. Evans[45] showed that the triplet 0,0 absorption bands of ethylenes lie in the region of 350 nm and Wilkinson and Mulliken[46] observed a singlet 0,0 band near 250 nm. Bearing in mind the presence of an "infinitely long" alkyl substituent in polyethylene, one may postulate the possibility of a corresponding shift of these bands towards the longest wavelengths observed in the phosphorescence spectra of polyethylene as 380 and 295 nm respectively. However, so far it has proved impossible to obtain reliable phosphorescence spectra of ethylene or its substituted derivatives. According to Potts[47], this may be caused by the capacity of the molecules of the ethylene type to rotate rapidly about the C=C bond after undergoing a transition to the triplet state. This entails an energy loss, the molecule reaches the point of intersection of the singlet and triplet terms and can undergo a radiationless transition to the ground state.

However, the majority of available facts are consistent with the hypothesis that carbonyl groups are the luminescence centres in polyethylene and polystyrene. This is suggested by the decrease of the luminescence yield on γ-radiolysis of the polymers (the number of double bonds then increases) and the increase of the luminescence yield on heating the polymer in air (the number of carbonyl groups increases).

Charlesby and coworkers[40,41] encountered considerable difficulties due to the inadequate sensitivity of the apparatus and the non-monochromatic nature of the exciting radiation. For example, the visual fluorescence observed for polytetrafluoroethylene could not be recorded with a spectrograph, which of course hinders a quantitative assessment of the observed phenomena.

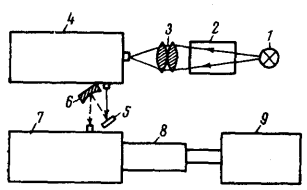


Figure 7. Diagram of apparatus for the recording of luminescence spectra: 1) DRL-500 mercury lamp; 2) water filter for the absorption of heat; 3) quartz condenser; 4) EMR-3 mirror monochromator; 5) specimen; 6) parabolic mirror; 7) SFD-2 monochromator; 8) FEU-19M photomultiplier; 9) U2-4 amplifier.

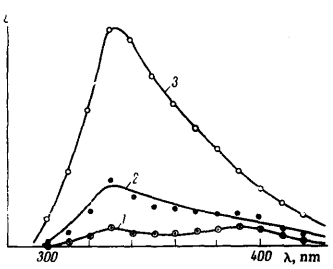


Figure 8. Effect of Tinuvine P (0.01 mole kg^{-1}) on the luminescence of polypropylene: 1) observed luminescence spectrum of the polymer with Tinuvine P; 2) luminescence spectrum of the polymer with Tinuvine P corrected for reabsorption and screening; 3) observed luminescence spectrum of the polymer without added Tinuvine P; L—luminescence intensity in relative units; the wavelength of the exciting light was 280.4 nm.

These difficulties were overcome after the construction from standard equipment of an apparatus (Fig. 7) for the investigation of low intensity luminescence with monochromatic excitation[37]. Fig. 8 shows a luminescence spectrum of atactic polypropylene obtained on this apparatus (Fig. 8, curve *3*). The spectrum of isotactic polypropylene is similar. These spectra make it possible to investigate quantitatively the form of the spectrum and the luminescence yield (see below).

It follows from the data quoted above that the fluorescence (reaction (2)] and phosphorescence [reactions (3) and (5)] processes may compete to a considerable degree with the photodissociation process (6), which is confirmed[40]

by the very low quantum yields of the radicals. We shall not consider here the role of the triplet states, because at room temperatures they are probably important only at very high light intensities (two-quantum processes[48]). The migration of energy [reaction (4)] will be examined below and now we shall consider the more important photodissociation reaction (6), which determines the nature of the radicals responsible for numerous secondary photochemical processes in light-induced ageing of polymers.

4. THE NATURE OF RADICALS FORMED ON ULTRAVIOLET IRRADIATION OF POLYMERS

The method most widely used at present to investigate the radicals formed on ultraviolet irradiation of polymers is electron spin resonance. As a rule these radicals are very reactive and they must be stabilised by a rigid polymeric matrix at low temperatures. Quantitative data concerning the accumulation of these radicals, their lifetimes, etc. at low temperatures cannot of course be used directly for kinetic calculations at room temperatures. However, these data are important for the understanding of the mechanism of light-induced ageing processes.

The processes involved in the formation of radicals in low-temperature photolysis (77°K) of polyethylene[41,49-51], polypropylene[49-54], poly(methyl methacrylate)[55], polystyrene, a number of polyolefins[49], and polyphenylmethylsiloxan[56] have been investigated in greatest detail.

When polyethylene was irradiated in air at room temperature, an ESR signal was not recorded[49]. At 77°K free radicals of two types were detected[51]: $\ldots CH_2-\dot{C}H-CH_2\ldots$, whose spectrum is the same as that of polyethylene subjected to ionising radiation and described in a number of studies[57-61], and the radical $\ldots CH_2-\dot{C}H_2$, arising on dissociation of the C–C bond of the polymer chain, which is not observed in the radiolysis of polyethylene. These two types of radicals are formed with approximately equal yields. Heating to 178°K transforms the initial ESR spectrum into a singlet, which has been tentatively attributed to a free radical of the allyl type produced from the radical $\ldots CH_2-\dot{C}H_2$ on dehydrogenation with the migration of the free valency along the polymer chain.

The results from the study of the ESR spectra of polypropylene irradiated with ultraviolet light differ from those obtained in the radiolysis of this polymer. The action of ionising radiation of polypropylene at a low temperature leads to the formation of the alkyl radical[62-69] $\ldots CH_2-\dot{C}(CH_3)-CH_2$. When the system is heated to room temperature, the eight-line spectrum of this radical is converted into a nine-line spectrum attributed to the allyl radical[64,66,67] $\ldots CH_2-\dot{C}(CH_3)-CH=C(CH)_3-CH_2\ldots$

γ-Irradiation of polypropylene at room temperature leads to the formation of a 17-line spectrum, attributed[66,67] to radicals of the allyl type. On the basis of new data, it is suggested that[70] this spectrum is due to an alkyl radical.

It follows from the results quoted above that, as a result of the action of ionising radiation on polypropylene, dissociation of C–H bonds predominates. The action of ultraviolet light on polypropylene at 77°K leads to the formation of a number of alkyl radicals.

Typical radical accumulation curves are presented in Fig. 9. The interpretation of the ESR spectra led to the discovery of the presence of the methyl radical[49,51,54] $\dot{C}H_3$ and the macroradicals $\ldots CH_2-\dot{C}H-CH_2\ldots$ and $\ldots CH(CH_3)-\dot{C}H-CH(CH_3)\ldots$ and also radicals with a free valence at the terminal CH_2 group, which are formed on dissociation of the C–C bond of the polymer chain: $\ldots CH_2-CH(CH_3)-\dot{C}H_2$.

The presence of the last named radical is most likely, since heating to 178°K converts the initial spectrum into a singlet, which, by analogy with polyethylene irradiation with ultraviolet light, was also attributed to an allylic radical arising on dehydrogenation of $\ldots CH_2-CH(CH_3)-\dot{C}H_2$.[51] The energy of ultraviolet light at a wavelength of 344.5 nm, consumed in the formation of a single free radical stable at 77°K, is 1.1×10^5 eV for polyethylene and 0.17×10^5 eV for polypropylene[51].

It is suggested[49,54,56] that the $\dot{C}H_3$ radicals can rotate rapidly in the polymer matrix even at liquid nitrogen temperature. This averages out the anisotropic broadening and yields the fairly well resolved ESR spectrum of polypropylene irradiated with ultraviolet light. The rotation frequency of $\dot{C}H_3$ in the polymer matrix is somewhat reduced (to about 30 MHz), and this accounts for the stabilisation of these radicals[51], which can exist for a week at 77°K.[49]

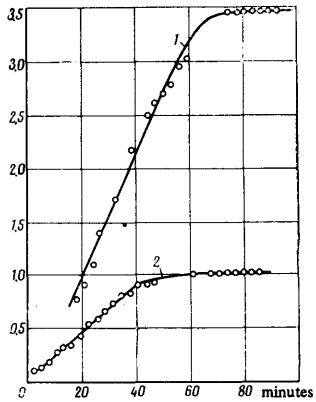


Figure 9. Curves for the accumulation of radicals in the photolysis of thermally oxidised atactic polypropylene: 1) irradiation in a quartz tube; 2) irradiation in a Pyrex tube (1 unit on the ordinate scale corresponds to 10^{16} particles).

When polypropylene was exposed to ionising radiation, the methyl radical was not detected. However, its intermediate existence is indicated by the presence of methane in the radiolysis products[71].

The irradiation of polyolefins containing short side chains results in the formation of free radicals of the corresponding side groups or methyl radicals if the side group contains a methyl[49]. Thus ethyl radicals $\dot{C}_2H_5$ and the macroradicals $\ldots CH_2-\dot{C}H-CH_2\ldots$ are formed in polybut-1-ene on irradiation with ultraviolet light; irradiation of poly-4-methylpent-1-ene leads to the formation of the same radicals as in polypropylene, while radicals similar to those in irradiated polyethylene are formed in polydodec-1-ene and polypent-1-ene.

In the low-temperature photolysis of poly(methyl methacrylate) (irradiation with the light of the DRSh-500 lamp) free radicals of two types were observed[55]: $\ldots CH_2-\dot{C}(CH_3)(COOCH_3)\ldots$, formed on dissociation of the main chain and long-lived only at the temperature of liquid nitrogen, and the radicals $\ldots CH_2-\underset{\displaystyle COOCH_3}{\overset{\displaystyle |}{\dot{C}}}H(CH_2)$, which persist at

room and higher (340°K) temperatures for several months. The authors believe that the radicals of the second type are produced from the radicals of the first type by the capture of a hydrogen atom from the methyl group by the free valence of the carbon atom in the polymer chain.

On ultraviolet irradiation of polystyrene, a broad singlet, tentatively attributed to phenyl radicals, was observed[49]. Free radicals of two types were identified by the ESR method in the low-temperature photolysis of polyphenylmethylsiloxan[56]: $\dot{C}H_3$ and $R-\dot{C}H_2$. The study of the kinetics of the accumulation of these radicals as a function of light intensity established that the relation between the rate of accumulation of the $\dot{C}H_3$ radicals and the intensity I_0 is $W_{CH_3} \propto I_0^2$ for low values of I_0 and $W_{CH_3} \propto I_0$ at high values of I_0, i.e. the relation becomes linear. For R = $\dot{C}H_2$, the rate of formation varies linearly with I_0 over the entire range of intensities investigated.

On the basis of these results, it was also concluded that the formation of the $\dot{C}H_3$ radical, requiring the dissociation of the Si–C bond, involves two quanta and the formation of $R-\dot{C}H_2$, requiring the dissociation of the C–H bond, involve one quantum. The authors assume that the absorption of the first quantum causes the transition of the molecule to an excited state in which the Si–C bond dissociates in such a way that the $\dot{C}H_3$ radical remains within the cage (one quantum at 300 nm is sufficient to dissociate the Si–C bond). This state of the radical in the cage presupposes a strong interaction with the residue of the molecule. Only the absorption of the second quantum enables the $\dot{C}H_3$ radical to leave the cage.

Strictly speaking a two-quantum process in photochemistry is thought to be one in which the absorption of the second quantum takes place from a photo-excited molecular level[48]. The quadratic relation between the rate of accumulation of radicals and light intensity can also be obtained when a molecule adsorbes two light quanta (a two-quantum mechanism), as in the case where the formation of radicals takes place via an intermediate compound (complex) produced under the action of the first light quantum followed by the absorption of a second quantum. In the latter case there is a two-stage mechanism. Therefore it is more correct to suppose that in the photolysis of polyphenylmethylsiloxan the generation of $\dot{C}H_3$ radicals involves a two-stage mechanism.

A two-quantum process is possible in photoinitiation via the CO group[32,41]. Thus thermoluminescence of polyethylene produced by ultraviolet light at 365 nm has been observed. This corresponds to a photon energy of 3.4 eV, which is insufficient for the ionisation of the carbonyl group. However, when the triplet state generated by the absorption of the first photon is long-lived (about 2 s), there is a possibility of absorption of a second photon before the molecule returns to the initial state by emitting a phosphorescence photon. The second photon raises the energy of the molecule above the ionisation limit and the CO group ionises.

As already mentioned above, in the group of polymers examined, the most probable centres absorbing ultraviolet light (at 300 nm) are impurity carbonyl groups in polyethylene, polypropylene, and other polyolefins, CO groups forming part of the monomer unit in poly(methyl methacrylate), and the phenyl rings in polymers such as polystyrene and polyphenylmethylsiloxan ($\lambda < 300$ nm).

Since the appropriate data are not available for the polymers, it is useful to employ data on the photodissociation of low-molecular compounds to elucidate the mechanism of the formation of radicals on ultraviolet irradiation of polymeric molecules in which the absorption centres consist of CO groups and benzene rings.

It may be assumed[30] that in the excited state the molecule has an additional valency compared with the ground state. In the $n\pi^*$ state (the $n \rightarrow \pi^*$ transition in the CO group) the molecule has an atomic valence and in the $\pi\pi^*$ state (the $\pi \rightarrow \pi^*$ transition in the benzene ring) the valence is delocalised over the entire molecule. The mechanisms of the reactions of molecules in these two states are different. In consequence of the delocalisation of the valence in the excited $\pi\pi^*$ state and in the absence of $\sigma-\pi$ conjugation, the utilisation of the valence is difficult and the molecules may break down simply due to the conversion of electronic energy into vibrational energy of a bond in the molecule. Then there may be two pathways for the conversion of the excitation energy into bond vibrational energy: the "direct" pathway when the electronic energy of the molecule is converted into the vibrational energy of the bond, the electron density of which changes at the instant of the transition (for example in the C–R bond of substituted benzene); the "indirect" pathway when the excitation energy is converted into the vibrational energy of the bond, but the electron density of the latter remains unchanged. The second pathway presupposes a pre-dissociation mechanism of the decomposition.

The mechanism of the photochemical decomposition of molecules in $n\pi^*$ states differs from the mechanism of the breakdown of molecules in $\pi\pi^*$ states. The presence of an atomic valence in the excited state leads to the possibility of intermolecular and intramolecular chemical reactions. In the intramolecular mechanism utilising the valence of the $n\pi^*$ state of the molecule the chemical bond linking atoms located in the same plane as the symmetry axis of the wave function of the n electron will dissociate. Thus in acetaldehyde in the $n\pi^*$ state the C–H bond will dissociate, in acetone the $C-CH_3$ bond, and in benzaldehyde the C–H or C–Ph bond.

Peters[38] calculated theoretically the electron densities of the bonds in formaldehyde for different electron transitions in the CO group. It follows from these data that the photolysis of low-molecular carbonyl compounds takes place via a stage involving the homolytic dissociation of one of the C–C or C–H σ bonds adjacent to the carbonyl group. Jellinek[23] points out that in the photolysis of low-molecular ketones caused by the absorption of light by the CO group two types of reactions may occur: (1) reactions with formation of free radicals with dissociation of the σ bond adjacent to the CO group:

$$R-CO-R_1 \xrightarrow{h\nu} \dot{R} + R_1\dot{C}O \rightarrow \dot{R} + \dot{R}_1 + CO;$$

(2) reactions accompanied by the dissociation of the C–C bond in the $\alpha-\beta$-position relative to the CO group; in this case radicals are not formed:

$$R-CH_2-CH_2-CH_2-CO-R_1 \xrightarrow{h\nu} RCH=CH_2+CH_3COR_1.$$

The formation of free radicals in the photolysis of monosubstituted benzenes and low-molecular carbonyl compounds has been confirmed experimentally by a tracer method[30]. Methyl radicals $\dot{C}H_3$ have been detected by the ESR method in the low-temperature photolysis of acetone and its aqueous solution[72]. However, the similarity to the photolysis of low-molecular compounds also fails to provide an unambiguous answer to the question of the site of bond dissociation in a polymer molecule on formation of free radicals. Among the polymers examined, polystyrene and polyphenylmethylsiloxan contain a benzene ring in the

monomer unit. According to the photodissociation mechanism of monosubstituted benzenes, it would appear that in the photolysis of polystyrene and polyphenylmethylsiloxan one might expect the photodissociation of the C–R bond of the benzene ring with formation of a phenyl radical and the counter-radical of the polymer molecule. The photolysis products should contain benzene or its derivatives. As already mentioned[49,50] the broad singlet in the ESR spectrum observed in the photolysis of polystyrene was tentatively assigned to the phenyl radical. The gaseous photolysis products at 77°K were not analysed.

However, in most studies on the photochemical degradation of polystyrene[26,73–75] it is suggested that the light-induced ageing of the polymer begins with the dissociation of a C–H bond at a tertiary carbon atom. As stated above, in the low-temperature photolysis of polyphenylmethylsiloxan the radicals $\dot{C}H_3$ and $R-\dot{C}H_2$ were detected, while the phenyl radical was not.

Possibly in the photolysis of polymers the excitation energy is transmitted from the benzene ring over larger distances than in monosubstituted benzenes causing the dissociation of remote bonds: C–H in polystyrene and $C-CH_3$ and CH_2-H in polyphenylmethylsiloxan.

In the photolysis of polymers with a C=O chromophoric group in the monomer unit one may expect, using the same analogy with the photolysis of low-molecular carbonyl compounds, the formation of radicals on dissociation of a bond adjacent to the CO group or in the $\alpha-\beta$-position relative to this group[23,30]. In the first case photolysis should be accompanied by the evolution of gaseous carbon monoxide.

In their study of the photolysis of polyamides at room temperature in a vacuum, Stephenson et al.[76] detected carbon monoxide among the gaseous photolysis products. In the photolysis of polyurethane, carbon monoxide was detected mass-spectrometrically[77]. Unfortunately the ESR spectra of the free radicals were not investigated in the first of these studies[76], while in the second[77] an ESR signal was observed but the radicals were not identified.

Evidently one may justifiably assume that in all these polymers the dissociation of the main chain takes place at bonds adjacent to the carbonyl group. In polyethylene, polypropylene, and other polyolefins the impurity carbonyl groups enter into the composition of the molecule, being located most probably in the main polymer chain: $\ldots CH_2-CO-CH_2-CH_2\ldots$ (polyethylene) and $\ldots CH_2-CH(CH_3)-CO-CH(CH_3)-CH_2\ldots$ and $\ldots CH_2-CO-CH_2-CH(CH_3)-CH_2\ldots$ (polypropylene).

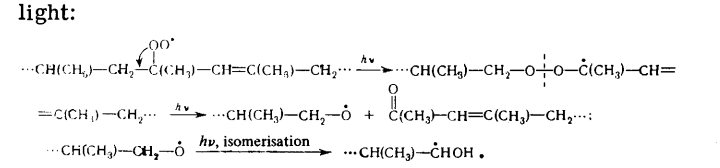
It has been suggested[51] that free radicals arising as a result of the dissociation of the main chain and with a free valence at the CH_2 group are produced in the photolysis of polyethylene and polypropylene: $\ldots CH_2-\dot{C}H_2$ for polyethylene and $\ldots CH(CH_3)-\dot{C}H_2$ for polypropylene. It may be supposed that in this case the C–C σ bond adjacent to the CO group dissociates. This photodissociation should be accompanied by the evolution of gaseous carbon monoxide. The gaseous products of the low-temperature photolysis of polyethylene and polypropylene were not analysed. At room temperature the photolysis of polyethylene in a vacuum and in a nitrogen atmosphere is accompanied by the evolution of hydrogen and methane[76]. Possibly, since the CO groups are present as impurities in the polymers investigated, carbon monoxide is difficult to detect experimentally because of its small amount.

However, the formation of the macroradicals $\ldots CH_2-\dot{C}H-CH_2\ldots$ in the photolysis of polyethylene and the radicals $\ldots CH_2-\dot{C}H-CH_2\ldots$ and $\ldots CH-(CH_3)-\dot{C}H-CH(CH_3)\ldots$ in the photolysis of polypropylene, and also data on the formation of radicals in polyolefins subjected to ultraviolet irradiation, when the side groups, or the methyls entering into the composition of the side group, mainly dissociate[49,50], suggest that in this case the photodissociation of polymers is not consistent with the mechanism of the photolysis of low-molecular carbonyl compounds. Possibly the excitation energy is transmitted over greater distances in the polymer molecule or the free valence migrates readily under the action of light.

Free radicals can change under the action of light and heat. In their study of the behaviour of radicals (generated by the γ-irradiation of a number of polymers at 77°K) under the action of the unfiltered light of a DRSh-250 lamp and heat, Milinchuk and Pshezhetskii[67,78,79] found that in many cases the radicals are destroyed and also that the ESR spectra of the radicals may change without a decrease in their concentration. In this case the destruction takes place at liquid nitrogen temperature where the possibility of mobility of different segments of the macromolecule may be virtually excluded.

The alkyl radical $\ldots CH_2-\dot{C}(CH_3)-CH_2\ldots$ formed initially in polypropylene at 77°K was converted on heating into the allyl type radical $\ldots CH_2-C(CH_3)-CH=C(CH_3)-CH_2\ldots$ and into the polyene radical $\ldots CH_2-\dot{C}(CH_3)-[CH=C(CH_3)]_n-CH_2\ldots$ The irradiation of allyl radicals with unfiltered light of a DRSh-250 lamp caused the reversion of the allyl radical to the alkyl radical. All the transformations of the radicals were deduced from changes in the hyperfine structure of the ESR spectra. The authors suggest that the mechanism of the formation of allyl and polyene radicals consists in the migration of the free valence of the alkyl radical along the polymer chain to a carbon atom adjacent to a double or conjugated bond. The migration is facilitated by the absorbed energy of the photon, which lowers the potential barrier to the migration of hydrogen atoms and the absorption is not necessarily associated solely with the chromophoric groups. Possibly the free radicals themselves absorb light. The mechanism of the migration of free valence in the macromolecule under the action of light and heat can explain the radical destruction processes at 77°K, the cross-linking and dissociation of the chain, the formation of double bonds, and the occurrence of conjugation.

Under the action of ultraviolet light, the peroxy-radicals derived from polypropylene are capable of isomerising to alkyl radicals[67]. The oxygen molecule is then incorporated in the polymer chain with formation of an –O–O– bond which is split by ultraviolet light with formation of a hydroxy-radical and a carbonyl group. Peroxy-radicals were accumulated by the oxidation of the alkyl radicals from polypropylene formed by γ-irradiation. The peroxy-radicals isomerised under the action of ultraviolet light with a maximum efficiency at 310–320 nm. The authors suggested that the peroxy-radical itself absorbs light:



Taking into account the possibility of the isomerisation of peroxy-radicals under the action of ultraviolet quanta from sunlight ($\lambda \simeq 300$ nm), one should note that the classical mechanism of oxidation via a stage involving the formation of hydroperoxide may not obtain in the photochemical oxidation of polypropylene, since the isomerisation is faster than the reaction $R\dot{O}_2 + RH \rightarrow$, which requires a favourable

encounter between the peroxy-radical and the hydrogen atom. Two mechanisms are possible for the reaction of $\dot{RO}_2$: isomerisation and the formation of hydroperoxide. This hypothesis requires experimental test.

Alkyl radicals obtained in the low-temperature photolysis or radiolysis of polymers are oxidised to peroxy-radicals on heating in an atmosphere of oxygen. The temperature of the oxidation of $\dot{R}$ to $\dot{RO}_2$ is 150° ± 10°K for polyethylene, natural rubber, and a number of saturated hydrocarbons, the recombination temperature being 210° ± 10°K.[80] The oxidation temperature of alkyl radicals was established on the basis of thermoluminescence data obtained on heating specimens irradiated with fast electrons. The thermoluminescence curves in the region of the phase transition temperatures show sharp rises, which are usually attributed to the lowering of the concentration of free radicals. The sharp rise ("flash") of thermoluminescence at temperatures 50–90 deg below the glass point, at which the concentration of radicals does not change, was attributed to the reaction of alkyl radicals with the oxygen dissolved in the specimen. Specimens subjected to preliminary evacuation did not show a rise of this kind in the thermoluminescence curve.

Since the temperature of the oxidation of alkyl radicals proved to be the same for polyethylene, natural rubber, and saturated hydrocarbons, it may be suggested that the reactivity of macroradicals is approximately the same and the temperature variation of the rate of oxidation of radicals is determined primarily by the increased mobility of segments of the chain and the penetration of oxygen to the site of the free valence.

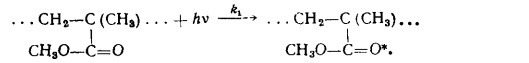
5. KINETICS OF THE FORMATION OF THE PRODUCTS OF LIGHT-INDUCED AGEING

To obtain the theoretical relation between the accumulation of any one product and the duration of exposure to light, it is necessary to set up a system of kinetic equations in accordance with the mechanism. The variation of the concentrations of the reactants and products depends on the nature of the photoinitiation and destruction of radicals and therefore the kinetic equations will be different for different polymers.

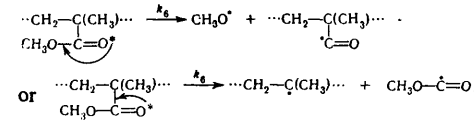
Poly(methyl methacrylate) (PMMA) and polystyrene (PS) constitute a group of polymers in which the absorption of light (stage 1) can take place in any monomer unit and in early stages of the reaction the number of absorbing centres may be regarded as almost constant. The absorbing centres in PMMA are ester carbonyl groups and in polystyrene phenyl rings if the wave-length of the initiating radiation is less than 300 nm. The nature of these groups and their positions determine the mechanism of the degradation of the absorbed energy.

In view of the large number of studies dealing with the light-induced ageing of PMMA,[23,55,81-88] the mechanism of the reactions occurring in this polymer may be regarded as sufficiently well established. We shall consider initially the photolysis of PMMA at a wavelength of 254 nm. The absorption of a photon is accompanied by the transition of a p electron of the carbonyl group from the non-bonding orbital of the oxygen atom to the anti-bonding orbital ($n \rightarrow \pi^*$ transition, see Fig. 6).

In this particular case stage 1, $S + h\nu \rightarrow S^*$, has the form



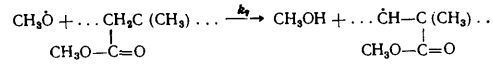
Then the excitation energy is transmitted by an intramolecular transition without emission to an ester C–O bond or a C–C bond, which leads to the photodissociation of the bond (stage 6 in the general mechanism, p. (149):



If each photon absorption step resulted in photodissociation the quantum yield φ of the photochemical reaction in light-induced ageing would be of the order of unity or even more than unity for a chain mechanism. However, at room temperature φ for a wide variety of polymers is of the order of 0.01 and frequently smaller by 2–3 powers of ten[23].

The mechanism which we propose for light-induced ageing clearly reveals the competing processes involving the degradation of electron excitation energy [reactions (2)–(6)] and permits a theoretical prediction of the quantum yield, provided that the corresponding rate constants are known.

The main products of the photolysis of PMMA are carbon monoxide, methanol, and methyl formate (see Fig. 10). Methanol is formed as a result of the secondary reaction



(stage 7 in the general mechanism, $P_f = CH_3OH$).

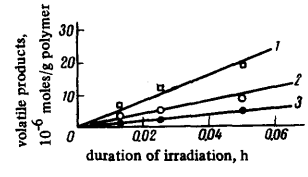


Figure 10. Amount of volatile products per gramme of PMMA as a function of the duration of irradiation at 30°C: 1) carbon monoxide; 2) methanol; 3) methyl formate.

The accumulation of methanol as a function of time is determined by the following set of equations

$$\frac{d(P_f)}{dt} = k_7(\text{M—M})(\text{R}), \tag{10}$$

$$\frac{d(\text{R})}{dt} = 2k_6(S^*) - k_8(\text{R})^2, \tag{11}$$

$$\frac{d(S^*)}{dt} = k_1 I_0(S) - [k_2 + k_3 + k_6](S^*). \tag{12}$$

Here round brackets denote the concentration of the corresponding reactant in cm^{-3}: (M–M), the concentration of hydrogen atoms combined with secondary carbon atoms, is almost constant and therefore $k_7(\text{M–M}) = \text{const.} = k'_7$; (S), the concentration of ester carbonyl groups is also almost constant, i.e. $k_1(S) = \text{const.} = k'_1$. Further, assuming that

the concentration of S^* corresponds to the steady state§, i.e. $d(S')/dt = 0$, we have from Eqn. (12)

$$(S^*)_{st} = \frac{k_1(S)I_0}{k_q}, \qquad (12a)$$

where $k_q = k_2 + k_3 + k_6$.

Similarly at the steady state¶ concentration (R), i.e. with $d(R)/dt = 0$, we have

$$(R)_{st} = \left(\frac{2k_6k_1}{k_qk_8}\right)^{\frac{1}{2}} I_0^{\frac{1}{2}} \sqrt{(S)}. \qquad (12b)$$

The accumulation of methanol is then determined from the equation

$$(P_f) = \int_0^t k_7(M-M)(R)\,dt = t\left(\frac{2k_6k_1}{k_qk_8}\right)^{\frac{1}{2}} k_7(M-M)I_0^{\frac{1}{2}}\sqrt{(S)}, \qquad (13)$$

i.e. the amount of methanol is proportional to the duration of exposure t, in agreement with Fig. 10.

The quantum yield of methanol is

$$\varphi_{CH_3OH} = \frac{(P_f)}{\Delta N}, \qquad (14)$$

where ΔN is the number of photons absorbed during time t. Assuming that radiation is only slightly absorbed in a layer ΔX, we have

$$\Delta N = I_0 t \cdot \kappa_1(S)\Delta X. \qquad (15)$$

Consequently

$$\varphi_{CH_3OH} = \left(\frac{2k_6k_1}{k_qk_8}\right)^{\frac{1}{2}} \cdot \frac{k_7\sqrt{(S)}}{I_0^{\frac{1}{2}}\,D}(M-M), \qquad (16)$$

where $D = k_1(S)\Delta X$ is the optical density of this layer.

It follows from the expressions obtained that, for a theoretical calculation of the rate of accumulation of the product and of the quantum yield with respect to this product, it is necessary to know a number of constants, which are not as a rule available. The data on the quenching constant k_q are particularly scarce and therefore it is difficult to assess the validity of the hypotheses concerning the mechanism of photolysis in this and other cases. However, the relations obtained make it possible to assess the nature of the process as a function of the given conditions. In particular, when account is taken of the quenching processes (2)–(6), the correct value of φ can be obtained with the aid of the constant k_q on substituting reasonable values of the constants. Unless k_q is taken into account, the discrepancy can amount to ten powers of ten.

It follows from Eqns. (13) and (16) that very important data on the mechanism of light-induced ageing can be secured by studying the kinetics of light-induced ageing at various intensities I_0 of the incident light.

In the case considered, the rate of accumulation of the photolysis products is directly proportional and the quantum yield inversely proportional to the square root of the intensity of the incident light. Experimental confirmation of this relation implies that the destruction of radicals takes place when two radicals meet (quadratic termination). However, such a mechanism of destruction in light-induced ageing of polymers is not the only one possible.

In the light-induced ageing of polystyrene, investigated in detail by Grassie[73,75] and other workers[26,74,89,90], a linear relation between the rate of formation of volatile and other products and the intensity I_0 of the incident light is observed both in photolysis and in photochemical oxidation. Precisely this fact is reflected in stage (8) of the general mechanism. Usually the destruction of radicals without collision with another radical (linear termination) in the condensed phase is disregarded. However, if account is taken of the fact that photochemical processes take place in a very thin surface layer, then, in view of the high mobility of hydrogen atoms and light $\dot{C}H_3$ radicals and the considerable inertia of macroradicals, it is quite possible that the light radical diffuses to the gas phase and therefore escapes from the reaction. The data quoted by Pudov and Taitarenko[91] indicate the occurrence of processes of this type.

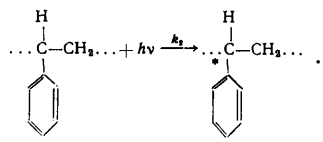
Grassie and Weir[75] investigated the photochemical oxidation of polystyrene films under the action of ultraviolet light (at 254 nm) at oxygen pressures up to 600 mmHg and temperatures of 28–57°C. Only water and carbon dioxide are formed in appreciable amounts from the gaseous products. At an oxygen pressure below 20 mmHg the rate measured from the absorption of oxygen is independent of the intensity I_0 of the incident light and at higher pressures it is proportional to I_0.

In accordance with the general mechanism of light-induced ageing the absorption of oxygen takes place in stage (9):

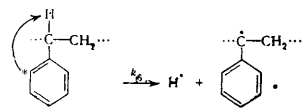
$$\frac{d(O_2)}{dt} = -k_9(O_2)(R), \qquad (17)$$

$$\frac{d(R)}{dt} = k_6(S)^* - k_8'(R), \qquad (18)$$

where (S^*) represents, as for PMMA, the steady-state concentration of excited states, with the difference that in polystyrene the absorbing centres are benzene rings:



As pointed out above, the electronic excitation energy during its dissipation is transmitted to the C–H bond of a tertiary carbon atom, which leads to the elimination of a hydrogen atom:



It is interesting that in the photochemical oxidation of polystyrene hydrogen is absent from the gaseous products, which is probably due to the rapid reaction $\dot{H} + O_2 \rightarrow H\dot{O}_2$.

As in PMMA, the steady-state concentration $(S^*)_{st}$ is determined from Eqn. (12):

$$(S^*)_{st} = \frac{k_1(S)I_0}{k_q}.$$

The steady-state concentration of the radicals $[d(R)/dt = 0]$ is determined from Eqn. (18):

$$(R)_{st} = \frac{k_6k_1(S)}{k_8'k_q} \cdot I_0.$$

Then, in accordance with Eqn. (17), the consumption of oxygen is determined by the equation

$$-\Delta(O_2) = \int_0^t k_9(O_2)(R)\,dt = \frac{k_9k_6k_1(S)}{k_8'k_q} \cdot (O_2)\;I_0t,$$

---

§The exact solution is $(S^*) = k_1(S)I_0(1-e^{-k_2t})/k_q$, i.e. $k \simeq 10^8\ s^{-1}$. To a high degree of accuracy after only one 1 s, $(S^*) = k_1(S)I_0/k_q$, i.e. (S^*) depends only on (S).

¶The exact solution is $(R) = (R)_{st}\tanh bt$.

i.e. in agreement with the experimental data at high pressures, the amount of oxygen absorbed is proportional to the concentration of O_2 and the light intensity I_0. In reality the situation is more complex and radical diffusion and gas diffusion processes play a considerable role. In particular, the solubility of oxygen in the polymer is low and proportional to its pressure[92]. Therefore at oxygen pressures below 20 mmHg the rate of absorption of O_2 is fully determined by the rate of diffusion and is independent of the light intensity. It is noteworthy that, depending on the conditions and the properties of the polymer, both linear and quadratic termination can occur in the system simultaneously and the variation of the rate of the process with intensity may be, generally speaking, of any kind.

Kinetic analysis of light-induced ageing is more complex for polymers where initiation takes place via absorbing groups of impurities, for example carbonyl groups. As already mentioned, polyethylene, polypropylene, and poly(vinyl chloride) belong to polymers of this type. In a number of studies[93-98] dealing with the light-induced ageing of polyethylene and polypropylene it has been shown that ultraviolet irradiation of such polymers is accompanied by the absorption of oxygen and the accumulation of oxygen-containing groups: carbonyl groups, hydroxy-groups, and others. The rate of absorption of O_2 by polyethylene is proportional to the square root of the intensity, i.e. quadratic chain termination takes place.

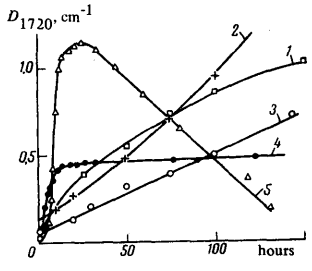


Figure 11. Kinetics of the accumulation of CO groups in the light-induced ageing of various polymers: 1) low-pressure polyethylene; 2) high-pressure polyethylene; 3) high-pressure polyethylene with a stabiliser (phenyl-α-naphthylamine + diphenylphenylenediamine + carbon black); 4) poly(vinyl chloride); 5) polyvinylbutyraldehyde.

The accumulation of CO groups is a complex function of time (Fig. 11, curves *1* and *2* for polyethylene) and depends on the properties of the polymer. In high-pressure polyethylene the number of CO groups rapidly increases with acceleration, while in low-pressure polyethylene the rate of accumulation of CO groups falls and after a certain time their accumulation is strongly retarded[96].

The difference between the nature of the ageing of high- and low-pressure polyethylene may be accounted for by their different degrees of crystallinity. It has been shown[18] that the rate of photochemical oxidation, determined from the absorption of O_2, is higher for crystalline polyethylene than for the pressed material, which is to a large extent amorphous. There is no doubt that this finding is related to the change in the rate of diffusion and solubility of oxygen on increasing the crystallinity of the polymer[92].

The amount of oxygen absorbed varies with time as a function of the crystallinity as well as the number of carbonyl groups.

The experimental data presented here are satisfactorily consistent with the general mechanism of light-induced ageing proposed above. Since the number of carbonyl groups is proportional to the amount of oxygen absorbed, it follows that $d(O_2)/dt = (P_0)/dt$, where (P_0) denotes in this case the concentration of initiating carbonyl groups. Since the carbonyl groups formed here behave at the same time as absorption centres, it follows that $(S) = (S_0) + (P_0)$, where (S_0) is the concentration of S at the initial instant of illumination at $t = 0$. Consequently $d(P_0)/dt = d(S)/dt$, i.e. the accumulation of P_0 is determined by the accumulation of S. In accordance with the general mechanism,

$$\frac{d(S)}{dt} = -k_1 I_0 (S) + k_2 (S^*_{st}) + k_9 (O_2)(R). \qquad (19)$$

As for PMMA, the steady-state concentrations $(S^*)_{st}$ and $(R)_{st}$ are determined by Eqns. (12a) and (12b) respectively. After substitution of $(S^*)_{st}$ and $(R)_{st}$ in Eqn. (19), we obtain

$$\frac{d(S)}{dt} = -k_1 I_0 \left(1 - \frac{k_2}{k_q}\right)(S) + k_9 \left(\frac{2k_6 \cdot k_1}{k_q\, k_8}\right)^{1/2} I_0^{1/2} (S)^{1/2}.$$

The differential equation obtained is a Bernoulli equation and can be solved analytically:

$$(S) = e^{-2p' I_0 t}\left[(S_\infty)^{1/2} e^{p' I_0 t} + (S_0)^{1/2} - (S_\infty)^{1/2}\right]^2, \qquad (20)$$

where $p' = (k_1/2)\,(1 - k_2/k_q)$ and (S_∞) is the limiting concentration of carbonyl groups at irradiation time $t \to \infty$:

$$S_\infty = \frac{2k_9^2\, k_6\, k_q}{k_1 (k_q - k_2)} \cdot \frac{(O_2)^2}{I_0}. \qquad (21)$$

According to solution (20), the concentration of CO groups increases steadily with time if $(S_0) < (S_\infty)$ and reaches a constant value (S_∞), which is in fact observed experimentally[96]. The time required for the attainment of the limiting concentration falls very rapidly (exponentially) with increasing intensity and strongly depends on the absorption (k_1) and quenching (k_2 and k_q) constants. The limiting concentration (S_∞) increases in direct proportion to the square of the concentration of oxygen and in inverse proportion to the intensity I_0.

The variation of (S_∞) with I_0 is particularly interesting It follows from Eqn. (20) that, when $(S_0) > (S_\infty)$, the concentration of CO groups must decrease with time during the initial period of the reaction until the limiting value (S_∞) is attained. Consequently if I_0 is small and (S_∞) large, carbonyl and other oxygen-containing groups will accumulate in light-induced ageing. Conversely, if I_0 is large, then S_∞ is small, and in the initial period the concentration of oxygen-containing groups should fall. This behaviour was confirmed experimentally in a number of studies[98,99] for the carbonyl groups of oxidised polyethylene (by infrared spectroscopy) and the hydroperoxy-groups of oxidised polypropylene (iodometrically). It is also interesting to note that, according to Eqn. (20), the rate of decomposition of oxygen-containing groups decreases with increasing oxygen pressure.

The conclusions based on the kinetic analysis of light-induced ageing of polyolefins are in general valid also for poly(vinyl chloride). It must be pointed out that a fairly large number of studies[100-106] dealing with this polymer are frequently contradictory, particularly as regards the composition of gaseous photochemical degradation products.

The paper by Reinisch[36], in which a general account is given of preceding studies and the experimental part was

carried out very carefully, must be regarded as the most reliable. Not even traces of water, carbon monoxide, and carbon dioxide, the formation of which was indicated, for example by Wilson[100] and others, were observed in the photolysis of poly(vinyl chloride). These products, together with hydrogen chloride, are characteristic of the photochemical oxidation of poly(vinyl chloride). The initiating centres are impurity CO groups both in the photochemical oxidation and in the photolysis of oxidised poly(vinyl chloride) (this in fact accounts for the evolution of the products enumerated above). In extensive oxidation and in the photolysis of non-oxidised poly(vinyl chloride) the absorbing centres are polyene structures.

6. THE MECHANISM OF THE SENSITISATION AND STABILISATION OF POLYMERS AGAINST LIGHT

Most of the studies on the light-induced ageing of polymers involve the search for effective additives, called light stabilisers, which inhibit the light-induced ageing and protect the polymer from the destructive effect of sunlight. However, so far there is no single point of view on the mechanism of light stabilisation, which hinders to a great extent the search for substances with protective activity and also the selection of light stabilisers for new polymers.

The most widely held is the view that the mechanism of light stabilisation reduces to the screening effect of the additive[4,85,107-109], i.e. it is suggested that the light stabiliser acts as a filter weakening the flux of ultraviolet radiation incident on the polymer. Attempts are then made[110] to establish a correlation between the absorption spectrum and the efficiency of the light stabiliser. If the absorption spectrum of the light stabiliser is known, it is not difficult to determine, in accordance with the Beer–Lambert law, the energy absorbed by a planar polymer specimen without an additive:

$$\Delta\epsilon_0 = Ft\sum_{\lambda_1}^{\lambda_2} I_{0\lambda}(1-e^{-\epsilon_{p\lambda}c_p d}), \qquad (21a)$$

and the energy absorbed by the same specimen with added light stabiliser (on the assumption that the absorbing centres are independent):

$$\Delta\epsilon_s = Ft\sum_{\lambda_1}^{\lambda_2} I_{0\lambda}(1-e^{-(\epsilon_{p\lambda}c_p+\epsilon_{s\lambda}C_s)d})\frac{\epsilon_{p\lambda}C_p}{\epsilon_{p\lambda}C_p+\epsilon_{s\lambda}C_s}. \qquad (21b)$$

Then the protective effect of the light stabiliser may be determined from the relation[111]

$$PE = \frac{\Delta\epsilon_0}{\Delta\epsilon_s} = \frac{\sum_{\lambda_1}^{\lambda_2} I_{0\lambda}(1-e^{-\epsilon_{p\lambda}C_p d})}{\sum_{\lambda_1}^{\lambda_2} I_{0\lambda}(1-e^{-(\epsilon_{p\lambda}C_p+\epsilon_{c\lambda}C_s)d})\frac{\epsilon_{p\lambda}C_p}{\epsilon_{p\lambda}C_p+\epsilon_{s\lambda}C_s}}. \qquad (21c)$$

Here $I_{0\lambda}$ is the intensity of incident light at a given wavelength λ, $\epsilon_{p\lambda}$ the molar extinction coefficient of the initiating groups of the polymer† (cm^2), C_p the concentration of these groups (cm^3), $\epsilon_{s\lambda}$ and C_s the corresponding values for the light stabiliser, F the surface area of the specimen, d its thickness, and t the duration of irradiation. Each term of the sums in the numerator and denominator represents the energy absorbed by the polymer at a given wavelength and the sums themselves define the energy absorbed in the wavelength range from λ_1 to λ_2. The functions $\epsilon_{p\lambda}C_p d = D_p$ and $\epsilon_{s\lambda}C_s d = D_s$ represent the optical densities of the polymer and the light stabiliser and may be determined experimentally by spectrophotometric measurements. The summation can be performed graphically.

It follows from Eqn. (21c) that, since $\Delta\epsilon_s$ is always less than $\Delta\epsilon_0$, PE is always greater than unity, i.e. almost any substance absorbing ultraviolet light at a given wavelength λ should exhibit a stabilising effect in irradiation with light having this wavelength.

Experimental tests[105,110] showed that this is not so. In general there is no correlation between the ultraviolet spectra of light stabilisers and their stabilising effect. For example, Schlimper[105] points out that, despite the broad and intense absorption band in the region of 300–400 nm, azo-compounds exhibit poor stabilising properties in relation to poly(vinyl chloride) and polyamides.

Direct comparison of the calculated value of the protective effect PE with experimental data on the light-induced ageing of different polymers shows[95,111] that the effect of additives cannot be explained merely by screening. Furthermore, benzophenone, which absorbs in the ultraviolet region, not only does not stabilise polyethylene film but actually accelerates its light-induced ageing[112], i.e. behaves as a sensitiser.

The attempt to eliminate completely the observed inconsistency between the absorbance of the light stabiliser and its protective effect on the hypothesis of photochemical reactions of the additive and its chemical interaction with the polymer[107-109,112] was also unsuccessful[95].

Recently a mechanism has been developed[37], according to which the protective effect or, conversely, the sensitising effect of the additive depends not only on the absorbance or photochemical reactions but also on the capacity of the given additive to participate in non-radiative transfer of electron energy as an acceptor or a donor. The derivation of Eqn. (21c) itself contains the assumption of the independence of the absorption by different centres, i.e. the possibility of the interaction of these centres is thereby assumed in principle.

The postulate of non-radiative energy transfer between molecules and photochemical processes is itself not new and has been elucidated in detail both theoretically and experimentally. In particular the work of the school of Vavilov and Terenin in this field should be mentioned[113-115].

The hypothesis of the occurrence of such processes in the light-induced ageing of polymers has been put forward by various workers, in particular by Schmitt and Hirt[111], but these questions have not been adequately elucidated in respect of light stabilisers. Probably this is due not only to the experimental difficulties but also to the deep-rooted concept of the screening mechanism for the effect of light stabilisers.

It has been suggested[37] that the protective effect of the light stabiliser, caused by the non-radiative energy transfer from the excited centre of the polymer molecule to the light stabiliser molecule, can be estimated from the efficiency of the quenching of the luminescence of the polymer by the given light stabiliser (in this case the additive behaves as an energy acceptor, denoted in the general kinetic mechanism by A). Indeed, since the luminescence intensity is proportional to the number of excited polymer molecules, the decrease of the intensity can characterise in principle the decrease in the number of molecules tending to decompose (stage 6), and therefore also the efficiency of the light stabiliser. Quenching may of course not be due solely to energy transfer and therefore the proposed characterisation of the protective effect may

†It is assumed that the absorption by other groups is low.

prove to be incomplete, like the characterisation based solely on the screening effect. The above hypotheses have been tested for common light stabilisers added to polypropylene[37].

Curve 3 in Fig. 8 represents the luminescence spectrum of polypropylene without additive excited by light at 280.4 nm. On addition of 0.01 mole kg^{-1} of 2-hydroxy-5-methylphenylbenzotriazole (Tinuvine P), an effective light stabiliser for polypropylene, the luminescence intensity L falls sharply (curve 1). It has been shown experimentally that L is proportional to the amount of light absorbed by the polymer.

It would appear that the decrease of luminescence intensity may be explained by the fact that, in consequence of the absorption of the initiating radiation by the light stabiliser, the energy absorbed by the polymer decreases by an amount

$$\Delta\epsilon = \Delta\epsilon_0 - \Delta\epsilon_s \qquad \text{[see Eqns.(21a) and (21b).]}$$

The additional decrease of L takes place as a result of reabsorption—the absorption of the light due to the luminescence by the light stabiliser. Consequently, when appropriate corrections are made for screening and reabsorption, curve *1* should coincide with curev *3*. However, these corrections yield only curve *2*, which lies much below curve 3. Hence it follows that in the presence of the light stabiliser some kind of quenching mechanism operates. In particular, such a mechanism may be energy transfer from polymeric molecules to light stabiliser molecules.

Thus in the study of light-induced ageing it is necessary to take into account both the screening effect of the light stabiliser and its protective acceptor effect. In the general mechanism of light-induced ageing the possibility of of the inhibiting effect of acceptor additives was taken into account in stage 4. Allowance for this effect is reflected in the appearance of yet another term, $k_4(A)$, in the denominator of the expression for the steady-state concentration of excited centres $(S^*)_{st}$ and the steady-state concentration of the radicals $(R)_{st}$, since the quenching constant is now defined by the equation $k_q' = k_2 + k_3 + k_6 + k_4(A)$. Since this quantity enters with a plus sign into the denominator, in the presence of a light stabiliser (acceptor A), $(S^*)_{st}$ and $(R)_{st}$ are smaller than in the polymer without additives. Correspondingly the rate of accumulation of oxygen-containing products will be lower, in agreement with experiment (Fig. 8, cf. curves *2* and *3*).

The screening effect of additives in the polymer was not taken into account the general mechanism, because in the preceding sections we did not deal with the problem of the effect of additives and in fact we assumed that the process takes place in a thin layer under the action of monochromatic light. Assuming that the incident light is *monochromatic* to simplify the treatment, we shall now introduce a correction for screening. In the presence of a light stabiliser of the acceptor type at a concentration (A) in a flat specimen of thickness d and with a surface area F, the number of excited states initiated during a time dt is, according to Eqn. (21b),

$$dS^* = I_0 F\, dt\,(1 - e^{-[\epsilon_S(S)+\epsilon_A(A)]d})\,\frac{\epsilon_S(S)}{\epsilon_S(S)+\epsilon_A(A)},$$

and the rate of initiation of excited states, expressed in $cm^3\ s^{-1}$, is defined by the following equation in the presence of A:

$$\Delta I_s = \frac{dS^*}{dF\,dt} = \frac{d(S^*)}{dt} = k_1' I_0(S), \qquad (22)$$

where

$$k_1' = \frac{\epsilon_S}{d[\epsilon_S(S)+\epsilon_A(A)]}\cdot(1 - e^{-[\epsilon_S(S)+\epsilon_A(A)]d}).$$

Here (S) and (A) are the concentrations of the absorbing centres of the polymer and acceptor respectively and ϵ_S and ϵ_A are their molar extinction coefficients, i.e. in the modification of Eqn. (21b) it was assumed that

$$C_p = (S),\ C_s = (A),\ \epsilon_{p\lambda} = \epsilon_S,\ \epsilon_{s\lambda} = \epsilon_A.$$

When $d \ll 1$, we obtain the following expression from Eqn. (22) on expanding the exponential term in series:

$$\Delta I_s = \epsilon_S\ I_0(S). \qquad (22a)$$

As was to be expected, for an infinitely thin specimen, we obtain the expression used earlier for the rate of initiation. To show that, it is sufficient to put $\epsilon_S = k_1$. The significance of the constant k_1 now becomes clear.

The general form of the kinetic equations does not change after the introduction of corrections for quenching and screening, but the constants have different values. For example, the accumulation of oxygen-containing products in initiation via impurity CO groups in the presence of a light stabiliser is defined by a relation analogous to Eqn. (20):

$$S = e^{-2p''I_0 t}\,(S_\infty^{1/2} e^{p''I_0 t} + S_0^{1/2} - S_\infty^{1/2})^2,$$

where the constants are

$$p'' = \frac{k_1'}{2}\left(1 - \frac{k_2'}{k_q'}\right) = \frac{1}{2}\frac{\epsilon_S}{[\epsilon_S(S)+\epsilon_A(A)]}(1 - e^{-[\epsilon_S(S)+\epsilon_A(A)]d})\left(1 - \frac{k_2 + K_4(A)}{k_q + k_4(A)}\right);$$

$$S_\infty' = \frac{2k_9^2\ k_6\ k_q'}{k_1'(k_q - k_2)}.$$

It is evident from the above expressions that, on introduction of additives into the polymer, the accumulation of products depends in a very complex manner on the concentration of the light stabiliser and the initiating centres and on the thickness of the specimen. Analysis of these relations may be greatly simplified for short time intervals.

This assumption is quite acceptable for the analysis of slow light-induced ageing processes. The relations obtained lead to the interesting finding that in very thin specimens the light stabiliser has no influence whatever if it exhibits only a screening effect. This conclusion is quite clear also on the basis of physical considerations; in a very thin layer the molecules of the light stabiliser cannot "eclipse" the absorbing centres of the polymer.

Furthermore, the additive may have a sensitising effect, i.e. may accelerate photochemical processes by the transfer of the energy absorbed by the additive to the polymer and can at the same time retard the light-induced ageing of thick specimens. A phenomenon of this kind was observed by Grassie[75] for the stabilisation of polystyrene by the widely known light stabiliser 2-hydroxy-4-methoxybenzophenone. In thin layers this light stabiliser accelerates the oxidation. In thick specimens the surface layer breaks down more rapidly on addition of the light stabiliser, but the main bulk of the polymer is protected from the action of light by the screening effect of the additive.

Thus, as a result of the interaction of two effects (screening and energy transfer) the same substance can exhibit stabilising and sensitising activity depending on the conditions. This has been clearly shown by Fox and Price[116]. It has been found that the characteristic features of the photolysis ($\lambda = 254$ nm) of PMMA and poly-α-methylstyrene dissolved in methylene chloride with

various additives can be accounted for by postulating the possibility of energy transfer between the additive and the polymer. The energy transfer can take place via both triplet and singlet levels. It has been observed that most additives, in particular the familiar light stabiliser 2,4-dihydroxybenzophenone, sensitise the photolysis of PMMA. The sensitisation, as for polystyrene films[75], is usually masked by the filtering effect of the additive. On the other hand, benzophenone has a stabilising effect because of the energy transfer from the PMMA molecule to the triplet level of benzophenone.

Two principles, on the basis of which light stabilisers can be selected for polymers, follow from the above findings. In the first place the light stabiliser must have an electron level which corresponds to a maximum in the absorption spectrum in the same region as the maximum in the luminescence spectrum of the polymer. This will ensure the greatest overlapping of the maxima and hence will give rise to the greatest possibility of energy transfer[113]. In the second place the light stabiliser must have an electron level which corresponds to a maximum in the absorption spectrum in the same region as the maximum in the absorption spectrum of the polymer.

In conclusion we may note that the laws governing the effect of light stabilisers are in the main valid also for the effect of dyes[5,6] on light-induced ageing of polymers.

7. METHODS FOR THE ACCELERATION OF LIGHT-INDUCED AGEING

In connection with the low rate of the light-induced ageing process under natural conditions (duration of tests up to 7.5 years[117]), methods of accelerated ageing have found wide application. For this purpose, a number of industrial and laboratory devices have been constructed.

In the development of apparatus for the artifical light-induced ageing the principal problem is of course the possibility of creating conditions resembling natural conditions to the maximum extent. In view of what has been said above, the difficulty of constructing such apparatus is quite evident. It consists in the fact that the requirements for rapid tests and for the maximum similarity to natural conditions are mutually exclusive. The point is that the creation of a source with a spectrum analogous to that of the sun does not by itself ensure that the data on light-induced ageing obtained with the aid of such a source can be applied under natural conditions, since the variation of the rates of various photochemical processes with intensity and hence the variation of the rate of the overall light-induced ageing process is frequently complex (see above).

For example, it has been shown by X-ray diffraction[18,119] that on ultraviolet irradiation the crystallinity of cellulose (cotton fibre) decreases steadily. It is then found that the decrease under the action of sunlight is smaller by a factor of only 3–5 than the decrease obtained by irradiation with the unfiltered light of a mercury lamp (200–800 nm), although the intensity in the latter case is higher by a factor of about 50 and a considerable part of the energy in the spectrum corresponds to the short-wavelength region.

If it is remembered that the emission intensity of artifical sources is frequently higher by a factor of hundreds and even thousands than that of solar radiation, it is quite evident that, for extrapolation to natural conditions, it is essential to have data on artificial light-induced ageing at different intensities and hence in the design of apparatus for accelerated ageing, provision must be made for the regulation of light intensity over a fairly wide range.

Another no less important requirement which must be taken into account in the design of apparatus for artificial light-induced ageing is the creation of a source with a spectral energy distribution resembling sunlight with sufficient precision particularly in the short-wavelength region. Only then can one transfer with adequate justification the results of artificial light-induced ageing to natural conditions. The presence of bands in the absorption spectra of polymers[73,77] by itself shows that the sensitivity of the polymer to radiation of different wavelengths (activation spectrum) will vary.

A particularly striking illustration of the dependence of the rate of light-induced ageing on the wavelength of ultraviolet radiation is provided by the data[36] in Fig. 4. The rate of change of the optical density (D) of poly(vinyl chloride), which is proportional to the amount of hydrogen chloride evolved, increases with increasing wavelength, passes through a maximum at 260 nm, and then falls to zero at 332 nm. The maximum is then found to coincide with the absorption maximum of polyene structures, which behave as activation centres for the light-induced ageing of poly(vinyl chloride).

It would appear that the problem of obtaining the required spectral distribution in the light source might be solved by studying the light-induced ageing under the action of monochromatic radiation at different wavelengths. The resulting rates of light-induced ageing might be adjusted to the solar spectrum by summing the rates of ageing at different wavelengths taking into account the intensity. However, in the general case such summation is not valid because of a kind of "synergism" of different wavelengths. For example, in the photolysis of poly(vinyl chloride) the number of photons required to obtain the same amount of hydrogen chloride with monochromatic irradiation is approximately 100 times greater than with polychromatic irradiation[35].

Apart from the conditions which must be satisfied by the emission, apparatus for artificial light-induced ageing must also make provision for the control of temperature and moisture content, which must correspond to the natural conditions. The available apparatus for artificial light-induced ageing as a rule only partially satisfies the conditions formulated above[77,98,118–122].

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Moscow Textile Institute
Institute of Chemical Physics, USSR
Academy of Sciences, Moscow

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The Electron Paramagnetic Resonance Method in the Study of Electron Phototransfer Reactions and Sensitised Photoreactions

V.E.Kholmogorov

This review examines critically almost all available results of studies of electron phototransfer reactions and sensitised photochemical reactions. The unique possibilities provided by the electron paramagnetic resonance method in the study of photochemical processes are demonstrated. New work on two-quantum photochemical reactions is examined in particular detail. The important part played by electron phototransfer reactions in photochemistry is also emphasised. The bibliography contains 161 references

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I. INTRODUCTION

The possibilities provided by the fruitful utilisation of the electron paramagnetic resonance method (EPR method) for the study of elementary photoprocesses in photochemically active systems, namely the detection and study of intermediate products of the free radical and radical-ion type, were demonstrated fairly convincingly in several hundred papers published in the period 1954–1966 in the Soviet Union and other countries. In a review[1] devoted to the application of the EPR method to the study of photodecomposition reactions (photodissociation and photoionisation), we examined the chief results and conclusions reached by various workers in the study of the mechanisms and types of phototransformations undergone by various compounds with the formation of free radicals as intermediate products. In most instances the EPR method was used as a supplementary method to confirm various conclusions regarding a photoprocess which had previously been detected or discovered by other methods.

The most interesting results have been obtained by using the EPR method to study electron phototransfer reactions (photo-oxidation, photoreduction, and photodissociative electron attachment) and the photosenitisation of chemical transformations of a substance under the influence of near ultraviolet and visible light. Terenin devoted considerable attention to this aspect, in connection with the investigation of methods for the utilisation of light energy in the model systems of a photosynthesising apparatus, particularly in connection with the study of the primary photophysical and photochemical transformations undergone by pigments, dyes, and related compounds[2]. The EPR method can undoubtedly give important information even for such complex photosensitive systems as photosynthesising organisms. The possibilities provided by the EPR method are illustrated in the present review for the example of many original studies of electron phototransfer reactions and photosensitised chemical transformations of substances.

II. THE EPR METHOD IN THE STUDY OF ELECTRON PHOTOTRANSFER REACTIONS

1. Photo-oxidation

The result of the reaction of a photoexcited substance with electron donors or acceptors may be elementary photoreduction or photo-oxidation, that is the acceptance of an electron by one component and its simultaneous loss by another component of the photosensitive system, that is electron phototransfer. In some instances the elementary photo-oxidation process, carried out in solid matrices at low temperature under the influence of ultraviolet light, is accompanied by the formation of free radicals. An example of a photoreaction of this kind is provided by the photo-oxidation of ions of the iron group or halide ions in acid medium in the presence of water[3–6]:

$$[Fe^{2+} + H_2O\,(H_3O^+)]_{H_2SO_4} \xrightarrow{h\nu} [Fe^{3+} + OH^-\,(H_2O) + H^\cdot]_{H_2SO_4}$$

$$[I^- + H_2O\,(H_3O^+)]_{H_2SO_4} \xrightarrow{h\nu} [I^\cdot + OH^-\,(H_2O) + H^\cdot]_{H_2SO_4}$$

The EPR method provides a direct and convenient means of detecting the hydrogen atoms formed in this reaction, since they have a characteristic spectrum consisting of two narrow lines at a distance of 508 Oe from one another. Under ordinary conditions, however, as a result of the high mobility and high reactivity of the hydrogen atoms, they cannot be obtained in sufficient quantities for detection. Published data show that in solid matrices, including ice, hydrogen atoms diffuse readily even at 77°K, and to detect them it is necessary to carry out the studies at 4.2°K and 20°K.[7] In frozen aqueous and concentrated sulphuric, phosphoric, and perchloric acids, however, the hydrogen atoms do not recombine at 77°K.[8] This property of acid solutions was used by Bubnov and coworkers[9,10] to detect the hydrogen atoms produced during electron phototransfer

from metal ions with variable valency (V^{2+}, Cr^{2+}, Fe^{2+}, Mn^{2+}, Co^{2+}, etc.) and various anions (I^-, N_3^-, SH^-, SO_3^{2-}, etc.) in aqueous medium.

For example, when solutions of $FeSO_4$ in sulphuric and phosphoric acids, frozen at 77°K, were illuminated, an EPR signal consisting of a doublet with splitting 507 Oe was detected. This indicated unambiguously that hydrogen atoms are formed in the electron phototransfer reaction. To confirm this conclusion, experiments were carried out with solutions containing heavy water. The triplet signal of atomic deuterium was then detected in the EPR spectrum.

In another experiment, these workers showed that not only ions, but also the neutral molecules of aromatic compounds, can take part in photoreactions of this type. When solutions of benzene in aqueous sulphuric and phosphoric acids, frozen at 77°K, were illuminated, they observed the EPR lines of hydrogen atoms and the EPR spectra of various radicals formed from benzene derivatives ($\dot{C}_6H_6^+$, $\dot{C}_6H_7$, $\dot{C}_6H_5$), produced according to the scheme:

$$[C_6H_6 + H_2O]_{H_2SO_4} \xrightarrow{h\nu} [\dot{C}_6H_6^+ + OH^- + H^\cdot]_{H_2SO_4}$$

$$\dot{C}_6H_6^+ + OH^- \rightarrow \dot{C}_6H_5 + H_2O; \quad \dot{H} + C_6H_6 \rightarrow \dot{C}_6H_7$$

The positive benzene radical-ion $\dot{C}_6H_6^+$ was identified by Carter and Vincow[11] in solutions of benzene in H_2SO_4 at 77°K, irradiated with ultraviolet light. The EPR signal with $g \simeq 2.0$ also consisted of the superposition of the EPR spectra of several radicals. The seven-component spectrum of the $\dot{C}_6H_6^+$ radical-ion was resolved when the irradiated solution was heated. It was found that the $\dot{C}_6H_6^+$ radical-ion is relatively stable in the range 85–170°K, whereas the other radicals disappear in this temperature range. The authors cited confirmed the identification of the EPR spectrum using deuterated benzene (C_6H_5D and C_6D_6). They also obtained the EPR spectra of hexamethylbenzene and hexaethylbenzene, photoionised under the same conditions, and measured the hyperfine interaction constants and g-factor for these radical-ions.

We also detected hydrogen atoms by the EPR method in an electron phototransfer reaction when diphenylamine in aqueous sulphuric acid was illuminated with ultraviolet light[12]. The hydrogen atoms were produced according to the scheme:

$$[Ph_2\dot{N}H + H_2O]_{H_2SO_4} \xrightarrow{h\nu} [Ph_2\overset{+}{N}H + OH^- + H^\cdot]_{H_2SO_4}$$

The formation of the positive diphenylamine molecular ion in this photoreaction was confirmed by the production of a coloured product with absorption maximum at 680 nm[13].

The formation of alkyl radicals during electron phototransfer was observed by Bubnov and coworkers[14] when solutions of oxalic, acetic, and chloroacetic acids in various alcohols (methanol, ethanol, propanol, and butanol), frozen at 77°K, were illuminated with ultraviolet light. To explain the results obtained, the authors cited made allowance for the fact that in the system studied, partial protonation of the alcohol may take place in the presence of acids. In fact, if a certain amount of ROH_2^+ and X^- ions are formed in a system of the type ROH + HX (where ROH is a molecule of alcohol, and HX a molecule of acid), irradiation of the system with ultraviolet light will lead to electron phototransfer from the X^- anion to the ROH_2^+ cation, with the formation of an alkyl radical $\dot{R}$ according to the scheme:

$$ROHH^+ + X^- \xrightarrow{h\nu} \dot{R} + H_2O + X$$

In all instances the concentration of alkyl radicals $\dot{C}H_3$, $\dot{C}_2H_5$, $\dot{C}_3H_7$, and $\dot{C}_4H_9$ amounted to 0.01–0.03 times the concentration of acid.

Intracomplex electron phototransfer, leading finally to the production of free radicals, was studied by the EPR method by Shagisultanova and coworkers[15]. They give the results obtained by measuring the EPR spectra of solutions of complexes of the type $K_3[M(C_2O_4)_3]$, where M = Co, Fe, Cr, and Mn, and also $[Co(NH_3)_6]_2(C_2O_4)_3$, in dilute sulphuric acid (0.5–20%) or in aqueous alcohol at 77°K, irradiated with ultraviolet light (PRK-7). The concentration of the salts was varied in the range 2.5×10^{-3}–10^{-1} M. The doublet EPR signal of hydrogen atoms was detected in the irradiated solutions. It was found that the nature of the coordinated ligand and complex-forming metal has a marked influence on the production of hydrogen atoms: the intensity of the hydrogen doublet is maximal for the axalato-complex of Fe^{3+}, and minimal for the oxalato-complex of Cr^{3+}. In addition to the hydrogen doublet, the central section of the EPR spectrum at $g = 2.0036$ showed a slightly asymmetric line, with weak lines on both sides of it, belonging to the formyl radical $H\dot{C}O$. The authors cited consider that the primary step in the action of quanta of ultraviolet light on these coordination compounds is electron phototransfer between the ligand and metal, leading to the production of doubly-charged metal ions M^{2+} (Fe^{2+}, Co^{2+}, etc.). The formation of hydrogen atoms takes place by the reduction of the water molecules present in the hydration sheath of the complex, as a result of the charge in charge $M^{2+} \rightarrow M^{3+}$. It is possible, however, that under the influence of ultraviolet light the coordination complex undergoes photodissociation with the liberation of oxalate ions, which then reduce the water: $C_2O_4^{2-} + HOH \rightarrow C_2O_4^{-} + \dot{H} + OH^-$, as takes place in $K_2C_2O_4$ and $[Co(NH_3)_6]_2(C_2O_4)_3$.

Tollin and Green[16] used the EPR method to study a reaction which is very important for the solution of the problem of photosynthesis, namely electron phototransfer from chlorophyll A to various quinones (9,10-phenanthrenequinone, p-benzoquinone, coenzyme Q_6, *p*-chloranil, and *o*-chloranil) in solution (EPA mixture 8 : 3 : 5) at 268–100°K in a vacuum. Irradiation of the solution with light absorbed only by chlorophyll ($\lambda \geq 550$ nm) produced an intense EPR signal (10^{15}–10^{17} unpaired electrons per ml) of the corresponding quinone radical-anion, that is the semiquinone ion, in accordance with the photoreaction scheme:

$$Chl + Q \xrightarrow{h\nu} Chl^* + Q \rightarrow \underset{\downarrow\uparrow \quad \downarrow\uparrow}{(Chl^+ \ldots Q^-)^*} \\ Chl + QChl^+ + Q^-$$

or:

$$Chl + Q \rightarrow (Chl \ldots Q) \xrightarrow{h\nu} \underset{\downarrow\uparrow \quad \downarrow\uparrow}{(Chl^+ \ldots Q^-)^*} \\ Chl + Q\,Chl^+ + Q^-$$

Tollin and Green[16] postulated as intermediate product of the photoreaction an excited charge-transfer complex (CTC), capable of dissociating to form the positive chlorophyll radical-ion (Chl^+) and the quinone radical-anion (Q^-). It was found that the degree of dissociation is determined by the electron affinity of the quinone, temperature, and the polarity and viscosity of the solvent. Only the signals of the quinone radical-anion were detected by the EPR method. The positive chlorophyll radical-ions could not be detected. This is not a specific feature of this photochemical system: the EPR spectra of chlorophyll radical-cations in solutions has not yet been obtained, even at low temperatures.

2. Photodissociative Electron Attachment

Allen and Ingram [17] and Azizova [18-21] showed that ultraviolet irradiation of aqueous solutions of aromatic aminoacids at 77°K leads to their photoionisation with the production of the EPR singlet signals of the aminoacid radical-cations and hydrated electrons. In the presence of aliphatic aminoacids (glycine, alanine, valine, lysine, glyclyglycine, and alanylalanine), which do not absorb ultraviolet radiation directly in the range 240–290 nm, the action of ultraviolet light ($\lambda > 240$ nm) produced the multicomponent EPR signals of the corresponding aliphatic aminoacids. Ultraviolet irradiation of aqueous solutions of aliphatic aminoacids in the absence of aromatic aminoacids does not produce EPR signals. To investigate the mechanism of the free radical formation, the EPR method was used to study aqueous solutions of a mixture of aromatic and aliphatic aminoacids, irradiated with ultraviolet light, at 77°K and various pH values. It was found that at pH 12, when the aliphatic aminoacids are present in the form $RCH(NH_2)COO^-$, irradiation with ultraviolet light does not lead to the formation of free radicals. The formation of radicals of the aliphatic aminoacids takes place in acid medium (pH 0.5) when the aminoacids are present in the form $RCH(NH_3^+)COO^-$. This fact, and the decrease in the quantity of hydrated electrons in the specimen with increase in the concentration of aliphatic aminoacids, suggest that the free radicals are produced as a result of electron phototransfer according to the scheme:

$$\text{tryptophan}^+\,(\text{tyrosine}^+) + R{-}\underset{\displaystyle NH_3^+}{\underset{|}{CH}}{-}COO^- \xrightarrow{h\nu} \text{tryptophan}^+\,(\text{tyrosine}^+) + R{-}\dot{C}H{-}COO^- + NH_3$$

Thus the deamination of the aliphatic aminoacids, detected from the SPR spectra, takes place as a result of an electron phototransfer reaction.

The study of the deamination of aliphatic aminoacids by means of coloured compounds which absorb visible light, for example riboflavine or dyestuffs (trypaflavine, Acridine Orange, eosin), is of considerable interest. The irradiation of aqueous solutions of Acridine Orange (10^{-3} M) in the presence of alanine (10^{-1} M) produces the quintet EPR spectrum of the alanine free radical [22,23].

A large variety of aminoacids, peptides, and di- and tripeptides containing free amine groups in different parts of the molecule (gly-ala, ala-gly, ala-gly-gly, gly-met, gly-ser, leu-gly, etc.) have been studied. In the presence of readily ionisable additives, deamination takes place as a result of the transfer of an electron to the NH_3^+ group of the molecule.

The formation of free radicals from alkyl halides by electron phototransfer from a readily ionisable additive to the alkyl halide ($RX + e^- \rightarrow \dot{R} + X^-$) was demonstrated by Claridge and Willard [24] for the tetramethyl-*p*-phenylenediamine + alkyl halide system (methyl, ethyl, propyl, and butyl halides) in 3-methylpentane at 77°K. Alkyl radicals were detected by the EPR method. The alkyl halides, which exhibit diffuse absorption bands in the region of 250 nm, readily undergo photodecomposition in 3-methylpentane at 77°K with rupture of the C–I (Cl, Br) bond under the influence of ultraviolet light of $\lambda \leq 254$ nm. Tetramethyl-*p*-phenylenediamine in organic glasses at 77°K has an absorption maximum at 320 nm [25] with molar absorptivity 3×10^3, and on irradiation in this range it readily undergoes photoionisation, as indicated by the production of the characteristic colour of its radical-cation [26] and the corresponding EPR spectrum [27-30]. In the presence of alkyl halides, the action of light of $\lambda > 300$ nm produces not only the EPR spectrum of the tetramethyl-*p*-phenylenediamine radical-cation but also the distinct EPR spectra of the alkyl radicals $\dot{C}H_3$, $\dot{C}_2H_5$, n-$\dot{C}_3H_7$, i-$\dot{C}_3H_7$, n-$\dot{C}_4H_9$, and i-$\dot{C}_4H_9$; these authors assume that the latter are produced by the dissociative attachment of electrons, removed by photoreactions from tetramethyl-*p*-phenylenediamine, to the molecules of the corresponding alkyl halides, which have a positive electron affinity. The relative yields of the radicals for equal integral exposures ($\lambda > 300$ nm) are as follows: CH_3Cl 100%, CH_3Br 30 %, CH_3I 10%, C_2H_5Cl 40%, C_2H_5Br 25%, C_2H_5I 5%, i-C_3J_7Cl 20%, n-C_3H_7Cl 10%, i-C_4H_9Cl 20%, and n-C_4H_9Cl 10%.

3. Photoreduction

Ketones act as photosensitisers for the oxidation of various alcohols [31,32]. Although the mechanism of the sensitisation of this photoreaction is not completely clear [33,34], it has been established that unstable sensitiser semiquinones and solvent radicals are formed. [35] The overall scheme for the chemical transformations is:

$$AQ + h\nu \rightarrow AQ^*; \quad AQ^* + RH \rightarrow A\dot{Q}H + \dot{R};$$

$$A\dot{Q}H \xrightarrow{pH>8} A\dot{Q}^- + H^+; \quad 2A\dot{Q}H \rightarrow AQH_2 + AQ$$

where **AQ** is the quinone, and **RH** the solvent.

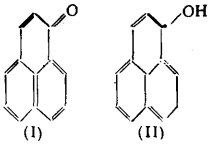
The production of semiquinones and radical-anions in this photoreaction was recorded from their optical absorption spectra by flash spectroscopy [33,36]. Their detection by the EPR method was of considerable interest.

Elschner and coworkers [37] used the EPR method to study the photoreduction of anthraquinone and its derivatives sodium anthraquinone-2,6-disulphonate, sodium anthraquinone-2-sulphonate, and 2,6-dichloroanthraquinone, at room temperature in alcohol. The structure of the EPR spectra of the semiquinones corresponds, as expected, to the interaction of an unpaired electron with two groups of equivalent protons. Solvent radicals were not detected, because of their low stability at room temperature.

The photochemical reduction of benzophenone in alcohols also involves an intermediate state [38]. Irradiation of a solution of benzophenone in propan-2-ol at −150° produced a structureless EPR signal, which disappeared when the temperature of the solutions was raised to −100°. Since the EPR signals in these experiments did not have a resolved hyperfine structure, their exact interpretation was difficult. Moreover, the experiment was carried out at −150°, and alcohol radicals were not detected.

Sharp and coworkers [39] used the EPR method to study the photoreduction of anthraquinone and benzophenone in methanol and propan-2-ol at room temperature and at low temperatures. EPR signals were not obtained when anthraquinone in methanol was irradiated at room temperature. When the temperature of the solution was lowered to −190°, however, a broad singlet without hyperfine structure was produced. The EPR signal disappeared with increase in temperature to −150°.

Under the influence of ultraviolet light, in degassed solvents such as methanol, ethanol, propanol, ethyl acetate, and acetone, which act as hydrogen donors, perinaphthenone (I) (absorption maximum at 359 nm)



(I) (II)

rapidly acquires a green colour ($\lambda = 650$ nm), which slowly

disappears in the dark[40]. It might be expected that this corresponds to the hydroxyperinaphthenyl radical (II), produced as a result of dehydrogenation of a solvent molecule by the photoexcited ketone. In fact, in degassed solutions of perinaphthenone irradiated with ultraviolet light (GEH-100 or Osram HBO-500 high-pressure mercury lamp) at 300°K, an intense EPR signal with hyperfine structure was obtained[41]. The hyperfine structure of the EPR spectrum of the radical formed is due to the interaction of the unpaired electron with the five protons of the equivalent hydrogen atoms in positions 3, 4, 6, 7, and 9, and with the three protons of the other equivalent hydrogen atoms in positions 2, 5, and 8. The same EPR signal was also obtained in solutions of perinaphthenone in dimethylformamide, irradiated with ultraviolet light, but the solution was not coloured. The green colour is apparently not due to the hydroperinaphthenyl radical.

Ayscough and Wilson, in a detailed study of the structure of aromatic ketyls[42-44] and radical-anions of aromatic nitro-compounds[45], used photoreduction of the starting materials (ketones and nitrobenzene derivatives) in concentrated alcoholic solutions of sodium methoxide or ethoxide at 20° in a vacuum as one method for obtaining negatively charged mono-ions.

The mechanisms by which these radical-anions are formed was investigated by Porter and Wilkinson[46]. On ultraviolet irradiation ($\lambda = 330$ nm), benzophenone is excited into a singlet state, from which it undergoes non-radiative transfer into a chemically active triplet state $Ph_2CO \xrightarrow{h\nu} Ph_2CO^* \rightarrow Ph_2CO_{T_0}$. Benzophenone in the triplet state removes a hydrogen atom from a suitable solvent, leading to the formation of the ketyl radical $Ph_2\dot{C}O_{T_0}$ + $RH \rightarrow Ph_2\dot{C}OH + \dot{R}$. In alkaline solutions, the radical-anion of the ketone (ketyl), familiar from its blue colour, is stabilised: $Ph_2\dot{C}OH + OH^- \rightarrow Ph_2\dot{C}O + H_2O$.

In Ayscough and Wilson's experiments, the source of ultraviolet light was a medium-pressure 250 W mercury lamp; the light from this lamp passed through a water filter to remove infrared radiation and was focussed by means of quartz lenses on the specimen situated in the resonator of the spectrometer. The photoreduction of benzophenone, 4,4-dichlorobenzophenone, and fluorenone, like electrolytic and chemical (by means of Na and K) reduction, led to the production of intensely coloured blue (benzophenones) or red (fluorenone) products. These coloured products gave well resolved spectra. These are the EPR spectra of the corresponding ketyls: Ph_2CO^-, Ar_2CO^-, and $C_{13}H_8O^-$. The maximal intensity of the EPR spectrum of the benzophenone ketyl is reached several seconds after the start of illumination. The ketyls of 4,4-dichlorobenzophenone and fluoroenone reached their maximal concentration 5–10 min after the start of illumination. The rates of disappearance of the ketyls in the dark correspond to the rates of their appearance. These spectra contain a larger number of components than the EPR spectra of the ketyls obtained by electrolytic reduction in acetonitrile. This is not due to better resolution of the spectrum as a result of narrowing of the individual components, however, but is due to a slight distortion of the distribution of the density of the unpaired electron in the ketyl as a result of a solvation effect. It is possible that an increase in the electron density of the unpaired electron in the aromatic ring is brought about by hydrogen bonding between the carbon–oxygen group of the ketyl and an alcohol molecule. Thus the ketyls in these systems should be regarded as Ph_2CO^-(solvated), Ar_2CO^-(solvated), and $C_{13}H_8O^-$(solvated).

The ketyls of benzaldehyde and acetophenone were obtained similarly. Their EPR spectra were observed several seconds after the start of ultraviolet irradiation. The short delay period is possibly due to the presence in the solution of uncontrolled impurities, which react with the radicals. For these ketyls, a solvation effect influencing the distribution of the density of the unpaired electron was also observed. It is revealed particularly clearly by comparing the splitting constants in alkaline methanol or ethanol solutions with the splitting constants in acetonitrile: all the splitting constants of the protons are decreased in acetonitrile. The stability of the ketyls also decreases in acetonitrile, due to the absence of a solvation sheath.

On ultraviolet irradiation of solutions of duroquinone in methanol, ethanol, or propan-2-ol in the presence of alkoxide ions, Cough and Symons[47] detected the EPR spectrum of durosemiquinone. Irradiation of solutions which did not contain alkoxide ions produced the EPR spectrum of the monoprotonated form of durosemiquinone[48]. Bridge and Porter[33] established that the mechanism of the formation of the radical-anions of quinones in alkaline solutions is the same as that in alkaline solutions of aromatic ketones. When strongly polar alcohols are replaced by less polar alcohols (quaternary pentanol), in which there is association of the radical-anion of the quinone (the semiquinone ion) with the alkali metal cation (Li, Na, or K) of the added alkoxide, the EPR spectrum of the semiquinone ion shows an additional structure, produced by the interaction of the unpaired electron with the nucleus of the alkali metal[49,50]. This indicates the formation of ion pairs. The magnitude of the hyperfine splitting is proportional to the effective density of the unpaired electron, which has 0.1–1% *s* character. By changing the polarity of the solvent, Cough and Symons altered the degree of association of the anion–cation pairs, and measured the rate constants for reactions of the type $M^+A^- \rightleftharpoons M^+ + A^-$ and $M^+A^- \rightleftharpoons A^-M^+$. Thus the EPR spectra of photoreduced aromatic ketones and diketones have been used to study not only solvation effects, but also the nature of ion association.

Ayscough and Wilson[44] detected solvation effects for the anions of aromatic nitro-compounds, obtained by photo-reduction in alcoholic solution in the presence of sodium methoxide or ethoxide. 16 para-substituted nitrobenzenes (*p*-alkoxynitrobenzenes, *p*-alkyl- and *p*-phenylnitrobenzenes, *p*-nitrobenzene alcohols, methyl *p*-nitrobenzoate, *p*-nitrobenzaldehyde, *p*-dinitrobenzene, and *p*-halogeno(Cl, Br, F)nitrobenzenes), *ortho*- and *meta*-fluoronitrobenzenes, and 2,6-dimethylnitrobenzene were subjected to photoreduction. The ease with which the aromatic nitro-compounds add an electron, and the stability of the resulting radical-anions, which give the solution a yellow-brown colour, permitted a detailed analysis of the EPR spectra and a comparison with the EPR spectra of the radical-anions of the corresponding nitrobenzenes, obtained chemically by reduction with glucose in alcoholic (ethanol or methanol) or aqueous-alcoholic medium in the presence of sodium ethoxide. The comparison showed that the spectra are identical. Most of the EPR spectra consist of three well resolved groups of lines, corresponding to the interaction of an unpaired electron with the nucleus of the nitrogen atom ($a_N = 7.9–14.8$ Oe), with the protons of the ring ($a_{H_o} = 3.1–3.5$ Oe; $a_{H_m} = 0.78–1.2$ Oe), and with the magnetic nuclei of substituents in the *para*-position ($a_p = 0.26–8$ Oe). Comparison of the EPR spectra of these radical-anions with the spectra of the same radical-anions obtained in an aromatic solvent shows that a proton-

donating solvent influences the distribution of the unpaired electron around the nitrogen atom, possibly as a result of the formation of a hydrogen bond with a solvent molecule.

Winkler and coworkers[51] showed by the EPR method that the radical-anions of various aromatic hydrocarbons can be obtained by photoreduction in the presence of phenyl-lithium. The action of ultraviolet light from a PL = 313 (70 W) high-pressure mercury lamp on solutions of biphenyl, terphenylene, naphthalene, phenanthrene, chrysene, pyrene anthracene, perylene, pentacene, and acenaphthene in diethyl ether at 20° gave coloured solutions, whose EPR spectra indicated the formation of radical-anions of the corresponding aromatic compounds. An additional hyperfine structure, due to the interaction of the unpaired electron with the lithium nucleus (^{7}Li, $I = 3/2$), was detected, indicating the existence of polyacene$^-$–Li$^+$ ion pairs under these conditions[52,53]. For example, the EPR spectrum of the anthracene radical-anion had the following characteristics: $a_\gamma = 5.35$ Oe, $a_\alpha = 2.45$ Oe, $a_\beta = 1.58$ Oe, and $a_{Li} = 1.70$ Oe. The mechanism of this photoreaction is being studied.

Charge transfer in molecular complexes, leading to the production of radical-anions, has been demonstrated by the EPR method for many charge-transfer complexes in the solid state. Lagercrantz and Yhland[54] showed that charge transfer can be induced by light in solutions of various organic charge-transfer complexes. An electron acceptor (chloranil, sym-trinitrobenzene, picryl chloride, or *m*-dinitrobenzene) was dissolved in an electron donor (tetrahydrofuran, *p*-dioxan, xylene, mesitylene, dimethoxyethane, or *o*-chlorophenol) and irradiated with ultraviolet light. Electron phototransfer was detected from the appearance of the EPR signals of the radical-anions of the corresponding electron acceptors. The maximal concentration of radical-anions amounts to 0.1% of the concentration of neutral molecules. The chloranil + tetrahydrofuran pair produces a single structureless EPR line, which disappears in the dark indicating that the phototransformations in the system are reversible. The EPR spectrum obtained on irradiation of the sym-trinitrobenzene + tetrahydrofuran pair has the hyperfine structure characteristic of the radical-anion of the electron acceptor.

Ward[55] observed the production of paramagnetism when a solution of nitrobenzene in tetrahydrofuran was illuminated, but the EPR spectrum of the paramagnetic centre contained a larger number of components than might have been expected for the nitrobenzene radical-anion. He was able to establish by means of deuterotetrahydrofuran that the additional splitting ($a_H = 0.38 \pm 0.04$ Oe) is due to the proton of the α-hydrogen of the tetrahydrofuran molecule. It may thus be assumed that under the influence of ultraviolet light, photoexcited nitrobenzene removes the α-hydrogen of the tetrahydrofuran molecule, and not the electron. The dehydrogenated tetrahydrofuran radical repidly dimerises or disproportionates, producing a non-paramagnetic compound. The conclusion that an uncharged nitrobenzene radical is produced on illumination of its tetrahydrofuran solution is confirmed by the absence of photoconductivity[56].

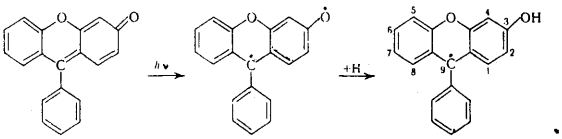
Tetracyanoethylene dissolves in most organic solvents to give solutions with an intense colour[57,58], due to the formation of a weak intermolecular complex with charge transfer[59-62] between the solvent molecule (the donor) and tetracyanoethylene (the acceptor). The production of a weak complex with charge transfer between tetracyanoethylene and tetrahydrofuran leads to the appearance of an absorption band at 318 nm[58]. The absorption band of the pyromellitic dianhydride + tetrahydrofuran complex lies in the range 330–385 nm[63]. Ward[56] showed that on illumination of their solutions the absorption band of the charge-transfer complex shows the EPR signals of the corresponding radical-anions: the eleven-component spectrum of the tetracyanoethylene radical-anion[64] and the three-component spectrum of the pyromellitic dianhydride radical-anion. The photogeneration of anion-radicals in these systems was confirmed by the production of photoconductivity. Analogous results were obtained on ultraviolet irradiation of solutions of tetracyanoethylene in methyltetrahydrofuran and *NN'*dimethylformamide. The photoreaction can be represented by the following scheme:

$$D + A \rightarrow D^{\delta+}A^{\delta-};\quad D^{\delta+}A^{\delta-} \xrightarrow{h\nu} D^+ + A^-\ .$$

As in the previous examples, proof of the existence of the positive tetrahydrofuran ion was not obtained.

Analogous results were obtained by Ilten and Calvin[65], who studied the photoinduced EPR signals and photoconductivity of solutions of tetracyanoethylene in tetrahydrofuran.

Bubnov and coworkers[66,67] used the EPR method to study the photoreduction of eosin. The photoreduction of eosin in the presence of a reducing agent involves the transformation of the dye into the leuco-compound. The mechanism of this reaction was previously studied by potentiometric and spectroscopic methods[68,69], and it was established that the reaction takes place in stages with the formation of intermediate product—the semiquinone of the dye. The lifetime of this intermediate product at room temperature amounts to several seconds. Illumination of eosin in pyridine in the presence of ascorbic acid (reducing agent) in fact leads to the production of the EPR signal of the corresponding semiquinone. The formation of the semiquinone in the photoreduction of eosin can be completely explained by Schenck's scheme[70].



eosin biradical semiquinone

The reversible photochemical reduction of chlorophyll by ascorbic acid is a model system for the photochemical stage of photosynthesis, in which light energy is stored in the photoproducts. Spectroscopic and electrometric measurements[71-73] have shown that the photoreduction involves the following elementary stages (Krasnovskii's reaction):

$$X + AH \xrightarrow{h\nu} X^* + AH \rightarrow X^{\cdot-} + \dot{A}H^+ \rightarrow \dot{X}H + \dot{A}$$

where X represents chlorophyll, and AH ascorbic acid.

The EPR method has been used to detect and study radical intermediate products formed on illumination of this model system[74,75]. Experiments on the photoreduction of chlorophyll and its analogues (pheophytin, haematoporphyrin, and magnesium phthalocyanine) were carried out in pyridine solutions in air and in a vacuum. The EPR signal produced in the illuminated solutions was found to be the same for all the pigments studied, and consisted of a doublet with a plitting equal to 1.8 Oe and $g = 2.004$. The spectra obtained belonged to the radical semi-oxidised form of ascorbic acid (monodehydroascorbic acid). In the system studied, the final stage involves the formation of a non-paramagnetic reduced form of the pigment and an

oxidised form of ascorbic acid. The EPR spectrum of the radical forms of the pigments could not be detected in any of the experiments, apparently because of their extremely high activity and correspondingly short lifetime in the system studied.

The semireduced semiquinone forms of the synthetic analogues of chlorophyll—the phthalocyanines—were detected by the EPR method during the dark reduction and photoreduction of these dyes in solutions in the presence of aliphatic amines or alkali metals[76,77]. Eigenmann[76] studied the photoreduction of copper phthalocyanine and phthalocyanine without metal in aqueous solutions in the presence of triethylamine and ethylenediamine. In the photoreduction of copper phthalocyanine, Cu^{2+} was converted into Cu^{+}, accompanied by a change in the intensity of the EPR signal. In the photoreduction of phthalocyanine without metal, which is a diamagnetic compound, a free radical whose EPR spectrum consisted of a narrow singlet was produced as intermediate product.

We showed[77] that the semi-reduced radical-ion form of Mg phthalocyanine and phthalocyanine without metal, produced by the reaction of the dye molecule with metallic sodium in tetrahydrofuran, is characterised by a structureless singlet EPR line with $g = 2.003$ and $\Delta H = 7$ Oe. These results show that the photoreduction of phthalocyanines takes place in an elementrary act involving the acceptance of one electron by the dye molecule.

Fujimori and Tavla[78] detected the formation of paramagnetic intermediate products in the photoreduction of chlorophylls *a* and *b* by hydroquinone in methanol under the influence of red light. Degassed solutions of $(4.5–4.9) \times 10^{-4}$ M chlorophyll and 10^{-2} M hydroquinone in methanol give two types of EPR signal on illumination. One has the hyperfine structure characteristic of the *p*-benzosemiquinone free radical, whereas the other is broad and is possibly due to the reduced form of chlorophyll. Measurements of the photovoltaic effect in these systems confirm the photoreduction of chlorophyll. The action of light apparently leads to electron phototransfer from hydroquinone to chlorophyll. Tollin and Banerjee[79] used the EPR method to study the reversible photoreduction of chlorophyll and pheophytin (*A* and *B*) by hydroquinone in alcohol solution in a vacuum (10^{-6} torr). They showed that the well resolved five-component EPR spectrum of benzosemiquinone is produced when a degassed solution of chlorophyll or pheophytin (7.3×10^{-5} M) and hydroquinone (2.2×10^{-2} M) in ethanol is illuminated with red light (duration of illumination from 30 min to 3 h). This photoinduced signal disappears very rapidly (< 1 s) on interruption of the illumination of the specimen, placed in the resonator of the spectrograph. Measurement of the optical absorption spectra of the solution before and after illumination showed that the electron transfer from the hydroquinone molecule to the photoexcited pigment is completely reversible. It was also found that oxygen effectively inhibits the oxidation of hydroquinone by reacting with the photoexcited pigment molecule[80,81].

It was found, however, that the addition of 0.1% pyridine (1.25×10^{-2} M) to this system increases the efficiency of the photoformation of the benzosemiquinone. Tollin and Banerjee suggest that this is due to the initial formation in solution of more readily oxidised non-paramagnetic complexes by the pyridinium ion and the hydroquinone anion, of the form $PyH^{+}...Q^{-}$. It is not excluded, however, that the addition of an organic base such as pyridine to the solution alters the pH of the medium and displaces the equilibrium for the reversible electron transfer towards the formation of the semiquonone.

The temperature dependence of electron transfer between hydroquinone and the photoexcited pigment molecule (chlorophyll or pheophytin) in the presence of pyridine was studied, and it was shown that electron transfer takes place even at −100°.

These results, and those given earlier, show that the photoexcited chlorophyll molecule, depending on the medium and its partners, may either take up or give up an electron with high efficiency, and this apparently determines its role in photosynthesis.

Rikhireva and coworkers[82,83] used the EPR method to detect chlorophyll molecules in the photoexcited triplet state, and also to study the free-radical forms of the pigment in ethanol solutions (5% HCl) at 77°K under the influence of visible light. Under these conditions a singlet EPR signal ($g \simeq 2$, $\Delta H = 9–11$ Oe) is produced in solutions of chlorophyll[83] and also of porphin and a number of prophyrins[84]. Similar singlet EPR signals were detected when solutions of chlorophyll in ethanol containing 20% water were illuminated with visible light at 77°K. The presence of reducing agents (ascorbic acid or phenylhydrazine) or oxidising agents (oxygen) in the solutions did not lead to intensification of the photoreaction at 77°K. Illumination of solutions of chlorophyll and pheophytin in ethanol, pyridine, piperidine, and 1 : 3 pyridine–ethanol mixtures at 300°K followed by rapid freezing ("fixation") of the solutions with liquid nitrogen leads to an increase in the intensity of the photoinduced EPR signals[85]. Under these conditions the concentration of paramagnetic photoproducts increases when oxygen, water, or a reducing agent are introduced into the solution. The authors cited[85] reached the following conclusion regarding the nature of the singlet EPR signal: the photoinduced EPR signal is due either to a charge-transfer complex formed by the photoexcited pigment molecule and the solvent molecule (with the participation of molecules of water and oxygen) or to a radical (radical-ion) form of the pigment.

Mauzerall and Feher[86] detected the EPR signals of the semireduced forms of various porphyrins, produced on illumination ($600 \leqslant \lambda \leqslant 700$ nm) of their degassed solutions in water, and also in aqueous glycerol at 25° in the presence of reducing agents. Three isomers of uroporphyrin and α,β-dihydroxyethyldeuteroporphyrin were studied. Ethylenediaminetetra-acetic acid, thiazolidine-4-carboxylic acid, NADH, and sparteine were used as reducing agents. The integral light intensity in the range 606–625 nm, corresponding to the long-wave absorption bands of the porphyrins, reached 10^{17} quanta $cm^{-2}s^{-1}$. Illumination produced singlet EPR lines of Gaussian form with $g = 2.0021 \pm 0.0001$ and $\Delta H = 5.4 \pm 0.2$ Oe. The EPR signal disappeared rapidly in the dark. Study of the kinetics of the disappearance of the EPR signal showed that the process involved in the disappearance of the paramagnetic centres is a second-order reaction. The processes taking place in these solutions can be described by the following scheme:

$$P + h\nu \xrightarrow{k_1} P^*$$

$$P^* \xrightarrow{k_2} P + h\nu_{fl.}\ (\text{heat})$$

$$P^* + R \xrightarrow{k_3} P^{\cdot} + R^{\cdot}$$

$$P^{\cdot} + P^{\cdot} \xrightarrow{k_4} P + \text{phlorin (dihydroporphyrin)}$$

$$R^{\cdot} + R^{\cdot} \xrightarrow{k_5} \text{product}$$

A possible reason for the absence of EPR signals from the radicals of the reducing agent ($\dot{R}$) may be that the rate constant $k_5 > k_4$, so that the steady-state concentration of $\dot{R}$ is too small for detection.

The formation of semireduced free-radical forms of various porphyrins on irradiation of their alcoholic solutions at 77°K by unfiltered light from a DRSh-1000 mercury lamp was detected by Gribova[87-91], who showed that the observed EPR spectrum of the free radicals consists of the singlet line of the free radical or porphyrin superimposed on the spectrum of the free-radical products of the decomposition of ethanol. It was also found that photoexcitation of porphyrins only in the long-wave absorption band (578 nm and 542 nm) leads to transfer of the chromophore molecule into the ground triplet state, but does not lead to the formation of free radicals. Comparison of the absorption spectra of a frozen solution of Mg etioporphyrin at 77°K before and after illumination with unfiltered light from a mercury lamp showed that in place of the characteristic absorption bands of porphyrin at 578 nm and 542 nm, an intense absorption band is produced at 686 nm, with a small maximum at 606 nm. Parallel qualitative comparison of the change in the concentration of the chromophore radical (singlet EPR line) and the absorption spectrum of the specimen with increase in temperature at 150°K showed that the decrease in the intensity of the absorption band at 686 nm corresponds to the decrease in the intensity of the EPR singlet line. According to these results, the absorption band at 686 nm can be assigned to the porphyrin free radical. As Gribova suggests, the porphyrin free radical may be produced as a result of the photoreduction of the chromophore molecule, existing in a high excited triplet state, by the solvent molecule.

4. Secondary Processes

The irradiation of salts of tervalent iron in alcoholic solutions with near ultraviolet or violet light leads to their reduction, with simultaneous oxidation of the solvent[92,93]. The basic elementary step in the photochemical reduction of tervalent iron in alcohols involves electron transfer within the complex:

$$Fe^{3+}Cl^- \xrightarrow{h\nu} Fe^{2+} + Cl^{\cdot}.$$

The chlorine atoms cannot be detected by the EPR method, but their formation is readily recorded from secondary processes—the chlorine atoms readily react with the alcohol, leading to the formation of free radicals:

$$RCH_2OH + Cl^{\cdot} \rightarrow R\dot{C}HOH + HCl.$$

Kryukov and coworkers[94] used the EPR method to detect and identify these radicals. To stabilise the alcohol radicals, the irradiation and the recording to the EPR spectra were carried out in methanol, ethanol, propan-1-ol, and propan-2-ol at 77°K. In all experiments a clearly defined EPR spectrum with hyperfine splitting was observed, indicating the presence of the free radical of the dehydrogenated alcohol in the system. The nature of the radicals is determined by the nature of the alcohol, and is independent of the nature of the iron complex.

Bazhin and coworkers[95], in a study of photoprocesses in an $H_2O + H_2SO_4 + FeSO_4$ mixture at 77°K in a vacuum, found that if the previously irradiated ($\lambda = 254$ nm) mixture is kept at 120°K and then cooled again to 77°K, the spectrum of the hydrogen atoms produced as a result of electron phototransfer disappears. This cannot be regarded as the result of recombination of the hydrogen atoms at 120°K, however. If the specimen is then subjected to irradiation again with visible light ($\lambda > 480$ nm), the doublet EPR signal of the hydrogen atoms is produced almost immediately on illumination. The formation of the "secondary" hydrogen atoms is observed if the second irradiation is carried out using red light ($\lambda > 600$ nm). These results show that the $H_2O + H_2SO_4 + FeSO_4$ photochemical system contains unique hydrogen atom traps, in which they are stabilised at 120°K. It is most probable that the hydrogen atoms at 120°K react with Fe^{2+} to form complexes of the type $(Fe^{2+}...H)$[96], which decompose under the influence of light with long wavelength ($\lambda > 260$ nm).

The use of the hydrogen atoms obtained in this way to study chemical reactions with various compounds at low temperatures is of considerable interest. Bazhin and coworkers[97] studied the reaction of hydrogen atoms with acetylene, ethylene, propene, allyl alcohol, and carbon monoxide at 90°K and 120°K. It was shown that at these temperatures the hydrogen atoms are capable of addition to these compounds with the formation of the corresponding radicals. Thus the reaction of hydrogen atoms with acetylene gives the vinyl radical $(H_2C=\dot{C}H$ (eight-component EPR spectrum with $a_\alpha = 16$ Oe, $a_\beta = 63$ Oe, and $a_{\beta_2} = 3.8$ Oe). The reaction of a hydrogen atom with ethylene gives the ethyl radical $\dot{C}_2H_5$. The reaction of a $\dot{H}$ atom with propene gives the isopropyl radical $CH_3\dot{C}HCH_3$. The reaction of a $\dot{H}$ atom with allyl alcohol $CH_2=CH-CH_2OH$ gives the radical $\dot{C}H_2-CH_2-CH_2OH$ (or $\dot{C}H_2-CH_2-CH_2OH_2^+$). The reaction of an $\dot{H}$ atom with CO gives the radical $H\dot{C}O$. Thus atomic hydrogen at 90–120°K can react with unsaturated compounds by addition to a double or triple bond or to a pair of unshared electrons (CO).

Whereas atomic hydrogen undergoes addition to unsaturated hydrocarbons at 90–120°K, in its reactions with saturated organic compounds in the same temperature range it removes a labile hydrogen atom. This was shown by Bazhin and coworkers[98], in a study of the reactions of atomic hydrogen with methanol, ethanol, propan-2-ol, ethylene glycol, isobutyric acid, malonic acid, and acetone. Bazhin and coworkers results[98] indicate that a "cold" $\dot{H}$ atom at 90°K is able to remove a labile hydrogen atom from the molecules of aliphatic alcohols, organic acids, and ketones.

Bazhin and coworkers[99] recently described the low-temperature reactions of hydrogen atoms with various aromatic compounds. They studied the reaction of atomic hydrogen in the $FeSO_4 + H_2O + H_2SO_4$ system irradiated with ultraviolet light ($\lambda = 254$ nm) with molecules of the following compounds: benzene, phenol, resorcinol, phloroglucinol, pyrocatechol, hydroquinone, guaiacol, 1,4-dimethoxybenzene, anisole, benzenesulphonic acid, benzyl alcohol, aniline, diphenylamine, and toluene. All the reactions at 90°K or 120°K produced radicals formed by the "attachment" of a hydrogen atom to the molecules of the aromatic compounds, characterised by an EPR triplet spectrum with a splitting of ~40–50 Oe for the protons of the $\diagdown CH_2$ group[100]. The additional splitting of the components of the triplet dependended on the position of the attached hydrogen atom relative to the substituent, and on the nature of the substituents. The EPR spectra of the radicals formed by the "attachment" of hydrogen atoms to the molecules of phenol, anisole, and benzenesulphonic acid show that 60–80% of the hydrogen atoms are attached in the ortho- or para-positions relative to the substituents. With resorcinol, the attachment of the hydrogen atom takes place chiefly in the ortho- or para-position relative to the OH groups. For pyrocatechol, hydroquinone, 1,4-dimethoxybenzene, and guaiacol, the EPR spectrum of the radicals formed by the "attachment" of a hydrogen atom consisted of a triplet of triplets, since in these radicals

the form of the EPR spectrum is independent of the position of attachment of the hydrogen atom. The observed EPR spectra for the radicals produced by the attachment of hydrogen atoms to the molecules of aniline, diphenylamine, and benzyl alcohol correspond to radicals with an H atom in the meta-position relative to the substituent.

Theoretical calculation[101] shows that the hydrogen atom should be attached chiefly in the ortho- or para-positions relative to the substituent, irrespective of the nature of the latter.

III. THE STUDY OF PHOTOSENSITISED REACTIONS OF ORGANIC COMPOUNDS BY THE EPR METHOD

1. Sensitised Photo-oxidation

The photo-oxidation and photoreduction of organic compounds, which require large quanta of energy, can be sensitised to the visible range of the spectrum by means of various dyes and pigments. A typical example of a photoreaction of this type is the photosensitised autoxidation of various aromatic compounds, studied by Ashkinazi and coworkers[102-104] by the EPR method.

When an ethanol solution of diphenylamine (10^{-2} M) at 293–295°K in the presence of chlorophyll *A* (10^{-5} M) and oxygen is irradiated with red light ($\lambda > 600$ nm), the colour of the reaction mixture changes in 10–15 min: the green solution first becomes reddish-brown, and then brown[102,103]. This is accompanied by a marked increase in the absorption in the range 400–560 nm. The same result is obtained when pheophytin *A* is used as senitiser. Prolonged irradiation of diphenylamine solutions freed from molecular oxygen does not change the absorption spectrum. The coloured product of the photoreaction was isolated in pure form. Its absorption spectrum is characterised by two maxima at 460 nm and 260 nm. The addition of a reducing agent (ascorbic acid, hydrazine, or hydroquinone) to a solution of this product instantaneously regenerates diphenylamine. This indicates that the autoxidation of diphenylamine sensitised by pigments gives a product which is not extensively oxidised. The authors cited[102,103] suggest that this product may be the diphenylnitrogen free radical $(C_6H_5)_2\dot{N}$. As confirmation of their suggestion, they give the EPR spectrum of the photoreaction product responsible for the colour; this spectrum consists of a triplet with component intensity ratio 1 : 1 : 1 and a splitting of 10–11 Oe. Ashkinazi and coworkers[103] suggest the following photoreaction scheme. A triplet molecule of the sensitiser reacts with the oxidation substrate (diphenylamine), removing an electron from it. This gives the diphenylamine radical-cation $[(C_6H_5)_2NH]^+$, which readily gives up a proton H^+ and is converted into the diphenylnitrogen radical $(C_6H_5)_2N$, which accumulates during the photoreaction. This scheme, however, ignores completely the part played by molecular oxygen in this photosensitised autoxidation. According to the above scheme, the photoreaction would take place with even greater efficiency under vacuum conditions, because of the quenching action of molecular oxygen on the triplet molecules of the sensitiser. Moreover, it is known that the diphenylnitrogen radical is extremely unstable in the presence of molecular oxygen and is rapidly converted in the dark into the diphenylnitroxide radical $(C_6H_5)_2\dot{N}O$, the EPR spectrum of which is extremely similar to the EPR spectrum of the diphenylnitrogen radical, showing only slight differences in the hyperfine interaction constants[105]. It may therefore be assumed that the accumulating free-radical product of the oxidation of diphenylamine, photosensitised by pigments (chlorophyll *A* or pheophytin *A*) is diphenylnitroxide. The diphenylnitrogen radical may be produced as a labile intermediate product of this photoreaction, as in the oxidation of diphenylamine by peroxo-compounds in the dark[106-108].

The formation of free-radical products was also detected by Ashkinazi and coworkers[103] in the autoxidation of *p*-phenylenediammonium chloride, photosensitised by pheophytin *A*, in alcoholic solution in the presence of molecular oxygen under the influence of red light. The photoreaction produced a reddish-yellow product (absorption maxima at 462 nm and 480 nm) with a singlet EPR signal and $\Delta H = 14$ Oe. The authors suggest that this product is the *p*-phenylenediamine radical-cation. The mechanism of the photoreaction is not discussed.

Ashkinazi and Dolidze[104] observed the autoxidation of α-naphthylamine, photosensitised by chlorophyll *A* and pheophytin *A*. In these experiments they observed a characteristic photo-after-effect: after the illumination of the system with red light was interrupted, the formation of an intensely coloured product (absorption maxima at 440 nm and 465 nm) continued for some time. The photoreaction does not take place in the presence of a reducing agent (ascorbic acid). EPR measurements showed that the photosensitised autoxidation of α-naphthylamine gives a free radical, the EPR spectrum of which consists of a singlet line with $\Delta H = 9$ Oe. The EPR signal disappears after several hours in the dark. Parallel measurement of the intensity of the absorption spectrum of the same specimen showed that the absorption increases so long as the EPR signal exists. This indicates that the free radical formed in the photoreaction takes part in a secondary reaction, leading to the production of a coloured product. The mechanism and nature of the intermediate product of the photoreaction have not yet been established.

The photo-oxidation of *NN*-diphenylamine, sensitised to visible light by eosin, in solution at room temperature was studied by Lagercrantz and Yhland[109] by the EPR method. They dissolved *NN*-diphenylamine in ethanol or pyridine (10^{-2} M), to which eosin was added (10^{-4} M). Illumination of the system with the visible part of the light from a xenon lamp (with a filter consisting of 5 cm of a 10% solution of $CuSO_4$ in H_2O) led to the immediate formation of a paramagnetic product, which disappeared under the influence of light in 5 min. This paramagnetic product is stable, however, in the dark in a vacuum. The EPR spectrum, recorded in the dark immediately after the attainment of the maximal concentration of the paramagnetic product, consisted of 37 components, situated in three main groups. It may be assumed that the photoexcited sensitiser (eosin) removes the hydrogen atom attached to the nitrogen atom of diphenylamine, leading to the production of the free radical $(C_6H_5)_2\dot{N}$, which is observed in the photoreaction. Unfortunately, the authors[109] did not study the optical absorption spectra of the photosensitive system before and after illumination. Precise identification of the paramagnetic product is therefore impossible.

Lagercrantz and Yhland[109] also detected the formation of a paramagnetic product in the photo-oxidation of phenothiazine, sensitised by eosin. Since the paramagnetic product is unstable in the dark, they were unable to obtain a complete well-resolved EPR spectrum. It was established, however, that the spectrum consists of three groups of lines, with a splitting of 9.5 Oe, due to the interaction of the unpaired electron with the nucleus of the nitrogen atom of phenothiazine. Each group contains a large number of

components. Although this EPR spectrum does not give complete information, it may be assumed that the phenothiazine free radical is produced as a result of the removal, sensitised by eosin, of a hydrogen atom from the bridging nitrogen atom.

The characteristic five-component EPR spectrum of *p*-benzosemiquinone was produced when alcoholic solutions of hydroquinone and *p*-benzoquinone (10^{-2} M) to which eosin had been added (10^{-3} M) were irradiated with visible light. The semiquinone appeared and disappeared as the light was switched on and off. Radicals were not detected when *p*-dimethoxybenzene was used as substrate. The reaction mechanism was not discussed. In these instances we undoubtedly have an example of oxidation or reduction of the substrate, photosensitised by the dye.

The EPR method has found application not only in sensitised photo-oxidation–photoreduction, but also in the polymerisation of a substrate, sensitised by dyes. Schenck and coworkers [110,111] showed that the cyclodimerisation of acenaphthalene (7×10^{-2} M), photosensitised by Bengal Rose (10^{-2} M), in methanol at room temperature gives as intermediate product a short-lived complex (adduct–product) of the photoexcited sensitiser molecule (Sens*) and acenaphthalene (Ace):

$$\text{Sens} \xrightarrow{h\nu} \text{Sens}^* \xrightarrow{+\text{Ace}} \text{Sens}^* \,\text{Ace} \xrightarrow{+\text{Ace}} \text{AceAce} + \text{Sens}$$

This complex is paramagnetic, and gives a three-component EPR signal, which differs from the EPR signal of the semiquinone of the sensitiser [66]. The authors cited point out that the photosensitised cyclodimerisation of acenaphthalene is an example of the photochemical transfer of energy from a sensitiser to the molecules of a substrate through a biradical complex [112].

2. The Photosensitised Decomposition of Organic Compounds

A unique position among photoreactions, sensitised to light of long wavelength, which have been studied by the EPR method, is occupied by the sensitised photodecomposition of saturated hydrocarbons, aliphatic alcohols, their esters, and various alkyl halides. These photoreactions provide examples of the chemical utilisation of light energy, transferred from a photoexcited sensitiser to substrate molecules (molecules of solvent or added substrate), in which is used in fairly high yield for the rupture of the weakest bond. There is now convincing proof that these photoreactions take place by a two-quantum mechanism with the participation of triplet molecules of the sensitiser (aromatic hydrocarbons, ketones, amines, dyes, and pigments).

Shelimov and coworkers [113-116] were the first to detect the sensitised formation of free radicals under the influence of ultraviolet light in transparent solutions of benzene in aliphatic hydrocarbons, frozen at 77°K. On ultraviolet irradiation ($\lambda = 254$ nm) in hydrocarbon media at 77°K, benzene is decomposed with rupture of a C–C bond of the benzene ring. Ultraviolet spectroscopy and gas chromatography showed that the product of the photochemical decomposition of benzene at 77°K is a substituted hexatriene.

Shelimov and coworkers [113-115] found by the EPR method that the reaction at 77°K gives not only hexatriene but also alkyl radicals (R̊), the formation of which did not fit into any of the schemes proposed to explain the formation of the substituted hexatriene. In their experiments, transparent solid solutions of benzene (1.8×10^{-3}–2.1×10^{-1} M) in methycyclohexane and 3-methylpentane were subjected to the action of light (PRK-7) at 77°K in a vacuum. Irradiation of these solutions with ultraviolet light ($\lambda > 230$ nm) produced free radicals, identified from the EPR spectra as methylcyclohexyl and 3-methylpentyl respectively. Alkyl radicals were also obtained by ultraviolet irradiation of hydrocarbon solutions of hexadeuterobenzene, toluene, ethylbenzene, isopropylbenzene, *o*-, *m*-, and *p*-xylenes, diphenylmethane, triphenylmethane [117], and naphthalene [118].

The fact that molecular hydrogen is formed on irradiation is extremely significant. The process leading to the simultaneous formation of alkyl radicals and hydrogen can only be the dehydrogenation of the aliphatic hydrocarbons, photosensitised by the aromatic hydrocarbons.

Shelimov recently † studied the dependence of the rates of formation of hydrogen (H_2) and alkyl radicals in solutions of benzene, toluene [117], and naphthalene [118] in 3-methylpentane on the intensity of the light. The quadratic dependence which he observed indicates that the photosensitisation is a two-quantum process. It should be noted that the rate of formation of the substiuted hexatriene is linearly dependent on the light intensity [121], that is this reaction is a one-quantum process. Shelimov and coworkers suggested [116] and demonstrated [117,122] that the intermediate state in the sensitisation is the triplet state of the aromatic hydrocarbon; in this state the hydrocarbon absorbs a second quantum of light with $\lambda < 370$ nm.

The ability of aromatic amines to bring about the photosensitisation of the dehydrogenation of aliphatic alcohols was observed by us in 1960 during an EPR study, carried out at the suggestion of A. N. Terenin, of the photoionisation of aromatic amines in an alcohol–ether mixture at 77°K. The publication of the results of this study [123] was stimulated by a paper published by Smaller [124] towards the end of 1962, on a study of the photodehydrogenating power of indole with respect to methanol at 77°K. In our experiments we studied solutions of the following amines: aniline, diphenylamine, triphenylamine, *p*-phenylenediamine, and tetramethyl-*p*-phenylenediamine; and the following heterocyclic compounds containing amine nitrogen: indole, carbazole, and 9,10-dihdroacridan. The solvents, which were purified by distillation, were methanol, ethanol, propan-2-ol, n-butanol, and 2-methylpropanol, and also diethyl, dipropyl, and dibutyl ethers. Control experiments showed that the solvents themselves do not decompose even on prolonged (3 h) irradiation with ultraviolet light ($\lambda \geq 300$ nm). Illumination of solutions of the aromatic amines and N-heterocycles (10^{-4}–10^{-1} M), frozen at 77°K, however, produced considerable concentrations of the free radicals of the solvent (alcohol or ether), formed by the removal of the labile α-hydrogen [123]. We made a detailed study of the dependence of this photoreaction on the duration and intensity of the ultraviolet irradiation, the spectral composition of the light source (DRSh-500), the temperature of the solution, and the presence of selective extinguishing agents for the triplet state of the sensitiser.

The inhibiting action of added naphthalene on the yield of the photoreaction in an ethanol solution of triphenylamine (carbazole) at 77°K provided convincing proof of the participation of triplet molecules of the amines in the photoprocess [123]. On the other hand, by means of the intermittent illumination method, we were able, like

† This study was undertaken by Shelimov and coworkers after the publication of papers by Bagdasar'yan and coworkers [119] and Terenin and coworkers [120], demonstrating the two-photon mechanism of the sensitised decomposition of aliphatic compounds.

Smaller for indole[124], to show that aromatic amines and N-heterocycles in the ground triplet state are not capable of dehydrogenating aliphatic alcohols at 77°K. The formation of free radicals took place only on irradiation and in the presence of triplet molecules of the sensitiser. We therefore suggested that the sensitisation photoprocess is a two-photon process[120]. An analogous suggestion that the sensitisation of the rupture of the C_α–H bond in methanol by photoexcited indole is a two-photon process was first put forward by Smaller[124]. In this instance the rate of formation of the radicals (dR/dt) should have shown a quadratic dependence on the intensity (I) of the light exciting the sensitiser, that is $dR/dt \sim I^2$. In fact, as shown by the measurements of Bagdasar'yan and coworkers[119,125,126] and results which we obtained[120], this relationship is observed fairly satisfactorily in experiments on the sensitisation by triphenylamine and diphenylamine of the dehydrogenation of methanol and ethanol at 77°K. It should be noted, however, that a quadratic dependence of dR/dt on I may be obtained both as a result of the absorption of two quanta of light by the sensitiser molecule (a two-photon mechanism) and also if the formation of free radicals of the solvent takes place through a photoactive intermediate compound (complex), which is produced under the influence of the first quantum of light and then absorbs a second quantum (a two-stage mechanism)[127-131].

To prove that the photoreaction is a two-photon process, it was necessary not only to obtain a quadratic dependence on the intensity of the light exciting the sensitiser, but also to prove that the absorption of the second quantum takes place in the photoexcited triplet-level of the sensitiser molecule (triplet–triplet absorption).

Bagdasar'yan and coworkers[125,126] studied the mechanism of this photoreaction by the method involving interrupted illumination of the specimens; by measuring the rates of the photoreaction with interrupted illumination ($t_{light} = t_{dark}$ = 0.5, 1.875, 3.75, and 7.5 s, duration of illumination 6–9 min) and continuous illumination (2 min) by light with λ = 313 nm, they estimated the characteristic lifetime of the intermediate state responsible for the absorption of the second photon in the diphenylamine + ethanol (5×10^{-4} M) and triphenylamine + ethanol (5×10^{-4} M) systems at 77°K. The agreement between this quantity (1.95–2.14 s for diphenylamine and 0.56–0.81 s for triphenylamine) and the lifetime of the sensitisers used in the triplet state (τ_{phosph} for diphenylamine = 1.9 s and τ_{phosph} for triphenylamine = 0.7 s[132]) must be regarded as providing quantitative confirmation of the earlier suggestion that the formation of alcohol radicals in these systems takes place as a result of an optical triplet–triplet transition of the amine molecule. Unfortunately, the positions of the short-wave and ultraviolet bands of the triplet–triplet absorption have not been established for aromatic amines and N-heterocycles. According to our data, they should lie in the range 260–340 nm, since it is this light which is photochemically active as the second quantum in the photoreactions involved in the dehydrogenation of primary and secondary alcohols at 77°K, sensitised by aromatic amines and N-heterocycles.

We obtained definite proof that the two-photon excitation of the sensitiser to high triplet states is a necessary stage in the sensitisation photoprocess in a study of the sensitised photodecomposition of t-butyl alcohol. t-Butyl alcohol $(CH_3)_3COH$ is an example of an alcohol which does not contain α-hydrogens. We showed[133] that by its sensitised photodecomposition it is possible, in the primary act of the photoreaction, to bring about rupture of a C–C bond with the formation of methyl radicals and the free radicals of the alcohol. When a solution of diphenylamine, triphenylamine, or indole (10^{-2}–10^{-3} M) in t-butyl alcohol at 77°K is irradiated with ultraviolet light ($\lambda \geqslant 320$ nm) corresponding to the long-wave edges of the absorption bands of the amines, the system after 5 min gives the EPR spectrum characteristic of the $\dot{C}H_3$ radical, and also an EPR spectrum identical to the spectrum of the radical of dehydrogenated propan-2-ol $(\dot{C}H_3)_2COH$. Similar spectra were observed on illumination ($\lambda \geqslant 300$ nm) of the solutions of naphthalene, phenanthrene, and biphenyl in t-butyl alcohol at 77°K, used as sensitisers. Of considerable interest in the rupture of the C–C bond in t-butyl alcohol, sensitised by dissolved naphthalene, for which the positions of the triplet–triplet bands, including the ultraviolet bands, are well known[134]. By illumination of specimens with monochromatic light from two sources, one of which (λ = 313 nm) was used to obtain high concentration of triplet molecules of naphthalene, whereas the light from the other corresponded to a given band of the triplet–triplet absorption of naphthalene, it was established that photochemically active conditions correspond to simultaneous subsidiary illumination of the solution by light with $\lambda > 365$ nm (the $T_0 \rightarrow T^*$ transition is brought about under the influence of light with λ = 415, 391, and 375 nm)[135].

Rupture of the C–CH_3 bond in t-butyl alcohol can be sensitised by means of various dyes. Acridine Yellow, Rhoduline Orange, and fluorescein (H^+ cation) were found to be extremely effective. The rate of production of free radicals shows a quadratic dependence on the intensity of the light exciting the dye[135,136]. By irradiation of solutions of the dyes by two light sources with different spectral compositions ($\lambda_1 > 400$ nm, $\lambda_2 < 400$ nm) it was established that the second photon is absorbed by a triplet molecule of the dye with its subsequent excitation to a high triplet state ($T_0 \rightarrow T_4^* - T_5^*$ -transition)[137,138].

Various biologically important compounds such as aromatic aminoacids (tryptophan, tyrosine, and phenylalanine) and nucleic acid bases (purine, adenosine, and guanosine), were found to have sensitising properties very similar to those of aromatic amines and N-heterocycles. Gribova and coworkers[87,89] studied the EPR of the triplet state of porphyrins and aromatic aminoacids (transition $\Delta m = \pm 2$) and found that during the ultraviolet irradiation of alcoholic solutions of aromatic aminoacids at 77°K the concentration of the latter in the triplet state decreases, with the simultaneous formation of free radicals of the dehydrogenated alcohol. The concentration of free radicals produced is proportional to the concentration of aromatic aminoacid molecules excited to the triplet state. A similar observation was made by Douzou and Ptak[139]. Azizova[18,20] found that brief (5 s) ultraviolet irradiation (unfiltered light from a DRSh-1000 mercury lamp) of a solution of tryptophan (2.5×10^{-3} M) in water in the presence of 2% ethanol at 77°K produces an EPR signal consisting of the superposition of the spectra of three paramagnetic products—the free radical $CH_3\dot{C}HOH$ (five-component spectrum), the positive tryptophan radical-ion, and an electron trapped in the matrix (singlet line). Subsequent prolonged irradiation of the solution by light with $\lambda \geqslant 320$ nm leads to a decrease in the intensity of the singlet EPR signal and to the appearance of components of the $\dot{C}H_3$ radical, produced as a result of photodecomposition of ethanol free radicals. The photosensitised decomposition of ethanol molecules also takes place in aqueous-alcoholic solutions of tyrosine and phenylalanine. The participation of the ground triplet state of aromatic amino-

acids in the photoreaction was confirmed by Gribova[87-91] in a study of the yield of free radicals obtained by interrupted and continuous irradiation of the specimens (tryptophan in ethanol, concentration 5×10^{-4} M) by light with the same intensity for the same total period of illumination. It was found that the yield of free radicals is smaller by a factor of 20 for interrupted irradiation (irradiation intervals 0.45 s, dark period 7 s). The participation of the excited triplet state of the aromatic aminoacids in the photoreaction was proved by the dependence of the yield of free radicals on the intensity of the incident light, which was found to be close to quadratic[89,91].

Helene and coworkers[140] found that purine, adenosine, and guanosine have a similar ability to sensitise the photodehydrogenation of aliphatic alcohols at 77°K. Ultraviolet irradiation ($\lambda > 250$ nm) of aqueous solutions of purine and adenosine (10^{-2} M) with 2% ethanol (0.35 M) at 77°K produced the five-component EPR spectrum of the $CH_3\dot{C}HOH$ radical, superimposed on a singlet EPR line‡. Subsequent irradiation of these solutions with visible light ($\lambda > 450$ nm) decreases the singlet signal, as a result of which the signal of the ethanol radical becomes more clearly defined. In aqueous solution containing 20% ethanol (3.5 M) or in pure ethanol solution, ultraviolet irradiation produced only the EPR signal of the ethanol radical $CH_3\dot{C}HOH$. At low intensities of the ultraviolet light, the rate of formation of the ethanol radicals remains unchanged with time and is proportional to I^2_{eff}, where I_{eff} is the intensity of the light absorbed by the molecules of the added sensitisers. At any moment of time, the rate of formation of the radicals is proportional to the concentration of triplet molecules of the sensitisers. The photosensitisation of the dehydrogenation of ethanol molecules by purine, adenosine, and guanosine evidently proceeds through an excited triplet state, produced by the two-photon photoexcitation of the sensitiser.

Irradiation of an ethanol solution of Mg etioporphyrin at 77°K by light from a superhigh-pressure mercury lamp (DRSh-1000) produces a large number of free radicals of the chromophore and ethanol $CH_3\dot{C}HOH$[87]. Gribova[88] showed by the EPR method that the irradiation of an ethanol solution of Mg etioporphyrin at 77°K by light with $\lambda =$ 578 nm, corresponding to the long-wave absorption band, produces only the EPR absorption due to molecules of the chromophore excited to the ground triplet state. The irradiation of frozen solutions by light with wavelength 248–365 nm for 5–10 min does not lead to the formation of free radicals, or produces them in very low yield. On simultaneous irradiation of solutions of Mg etioporphyrin in ethanol at 77°K by light from two sources (two DRSh-1000 lamps) with different spectral compositions, the yield of free radicals increases sharply (by a factor of 5–20) when the first source contains light of wavelength $\lambda = 578$ nm, leading to the formation of triplet molecules of the chromophore, and the second source has $\lambda < 322$ nm. Increase in the energy quantum from the second source increases the rate of formation of the free radicals. The EPR spectrum in this instance consists of the superposition of a single line due to the chromophore radical and a low concentration of free radicals of the alcohol $CH_3\dot{C}HOH$. From these results obtained by Gribova, it follows that the energy of a quantum of light of $\lambda = 578$ nm, absorbed by Mg etioporphyrin, is sufficient only for the excitation of its molecules to the ground triplet state, but is insufficient for the formation of free radicals; in the ground triplet state the chromophore is photochemically inactive in an ethanol matrix at 77°K. A high-energy quantum of light ($\lambda =$ 248–365 nm), however, is also insufficient for the dehydrogenation of ethanol in the absence of chromophore molecules excited to the ground triplet state. Free radicals of the chromophore and matrix are formed only on simultaneous irradiation by two quanta of light of $\lambda = 578$ nm and $\lambda < 322$ nm. The addition of glutathione, which was found to be a selective extinguishing agent for the triplet state of the chromophore, to an ethanol solution of Mg etioporphyrin led to a sharp decrease in the yield of radicals[89,91]. The participation of the ground triplet state as an intermediate state in the photochemical dehydrogenation of ethanol was proved by the dependence of the yield of free radicals on the intensity of the incident light; this dependence was found to be close to quadratic[89,91]. Direct proof of the participation of the ground triplet state of Mg etioporphyrin as an intermediate state in the photodehydrogenation of ethanol at 77°K was obtained by determining the influence of interrupted illumination on the yield of free radicals[90]. The solution was illuminated by unfiltered light from a DRSh-500 mercury lamp. The experiment was carried out at low light intensities. The periods of illumination were 1.8×10^{-2}, 9.0×10^{-3}, and 6.0×10^{-3} s, that is much less than τ_{phosph} for Mg etioporphyrin ($\tau_{phosph} = 1.83 \times 10^{-1}$ s [141]). The dark periods amounted to 1–2 s. Comparison of the yields of radicals for continuous and interrupted illumination for the same total periods of illumination showed that the concentration of radicals for continuous illumination is greater by a factor of 16 than for interrupted illumination with illumination intervals of 1.8×10^{-2} s, and greater by a factor of 25–30 than that for interrupted illumination with illumination periods of 9×10^{-3} s; this agrees with theoretical calculation and shows that a short-wave light quantum is absorbed by the chromophore molecule in the ground triplet state.

We noted in our first paper[123] that naphthalene, acting as sensitiser, can bring about the dehydrogenating of primary aliphatic alcohols at 77°K, but the yield of the photoreaction is lower by two orders of magnitide than that observed when aromatic amines and heterocycles with an amine group are used as sensitisers. Siegel and coworkers[142,143] made a detailed EPR study of the photodehydrogenation of ethanol, diethyl ether, and methylcyclohexane at 77°K, sensitised by naphthalene. They found that the rate of dehydrogenation also shows a quadratic dependence on the intensity of the light exciting the naphthalene. They also established that radiation with wavelength 270–300 nm is effective for the excitation of naphthalene molecules to the ground triplet state. Photochemical activity was observed, however, when the specimens were irradiated simultaneously with this radiation and by light of wavelength 250–260 nm. The naphthalene acting as sensitiser was not used up to a significant extent in the photoprocess. The observed decrease in the intensity of the EPR signal of the triplet molecules of naphthalene (transition $\Delta m = \pm 2$) was related to the decrease, by a factor of more than 100, in the lifetime of naphthalene in the triplet state as a result of the extinguishing action of the free radicals of the dehydrogenated solvent, produced on illumination. The formation of radicals of the solvent was not observed on illumination of non-degassed solutions of naphthalene at 100°K, that is under conditions where the

‡ In aqueous solutions of purine, adenosine, and guanosine, ultraviolet irradiation ionises the molecules $Pu \xrightarrow{h\nu} Pu^+ + e$. The singlet EPR signals actually consists of the signal of the Pu^+ radical-cation and the signal of electrons trapped by the matrix at 77°K.

steady-state concentration of the triplet molecules of naphthalene is low as a result of extinction by diffusing molecules of oxygen. The rate of appearance of free radicals of the dehydrogenated solvent increases significantly at 77°K when naphthalene is replaced by completely deuterated naphthalene, since the lifetime of the latter in the triplet state is greater by a factor of 5. [144] These results show that the groud triplet state of the naphthalene molecules is an intermediate state in the photosensitisation. The quadratic relationship shown by the rate of formation of the free radicals, and the fact that the range of photochemically active wavelengths coincide with the short-wave band of the triplet–triplet absorption of the naphthalene molecule ($\lambda \simeq 260$ nm)[134], enabled Siegel and Eisenthal to postulate that the sensitisation is a two-photon process, in which the final stage is the excitation of the molecule of the sensitiser (naphthalene) to a high triplet state.

West and coworkers [145,146] made a detailed optical study of the decomposition of alkyl iodides in hexane and ethanol at 300°K, photosensitised by naphthalene. We used the EPR method to study the primary processes taking place during the ultraviolet irradiation of solutions of alkyl iodides (methyl iodide and ethyl iodide) containing various sensitisers (diphenylamine, triphenylamine, naphthalene, biphenyl, phenanthrene, and benzophenone) at 77°K, and found that the sensitisation of the rupture of the C–I bond of the alkyl iodides is a two-photon process [147–150]. The spectral dependence of this photoreaction was studied for specimens containing naphthalene as sensitiser. The specimens were irradiated by two light sources. The light from one of these sources (a DRSh-500 superhigh-pressure mercury lamp) was filtered through a filter which picked out the 313 nm mercury line, necessary for the excitation of naphthalene to the triplet state. The light from the other source (DRSh-250), which was combined with an SZS-22 filter, contained the 365, 404, and 408 nm mercury lines, falling in the known range of the triplet–triplet absorption of naphthalene [134]. It was established beforehand that each source taken separately did not bring about the photodecomposition of the alkyl iodides at 77°K. Photodecomposition took place, however, under the simultaneous influence of both sources.

Similar experiments were carried out with specimens containing the dyes Acridine Yellow, Rhoduline Orange, fluorescein, and porphyrins as sensitisers. The only difference was that visible light ($\lambda > 400$ nm) was used to excite the dyes to the triplet state, and the triplet–triplet transitions were brought about under the influence of ultraviolet light with $\lambda < 400$ nm. The absorption spectrum of the triplet molecules of the dyes contains diffuse bands in the near ultraviolet range [137,138].

Siegel and Judeikes [151] used the EPR method to detect the decomposition of polydimethylsiloxane $[-O-Si(CH_3)_2-O-]_n$, photosensitised by naphthalene at 77°K. Methylsiloxanes are very stable to near ultraviolet light ($\lambda > 240$ nm) since neither the O–Si–O group not the $Si-CH_3$ group have absorption bands in this spectral range. In the presence of naphthalene, however, polydimethylsiloxane is decomposed at 77°K by light of $\lambda > 240$ nm, and the EPR spectrum shows two types of radical $\dot{C}H_3$ and $[-O(\dot{C}H_2)Si(CH_3)-O-]$. The quadratic dependence of the yield of $\dot{C}H_3$ radicals on the intensity of the incident light indicates that the sensitisation is a two-photon process. The naphthalene molecule is transferred to the ground triplet state under the influence of protons with $\lambda \leqslant 313$ nm. The simultaneous action of protons with $\lambda \simeq 250$–260 nm converts the naphthalene molecule into a high triplet state.

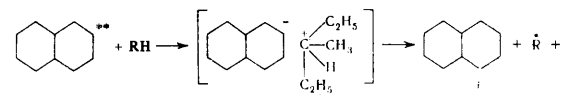
These results of the study of the photosensitised decomposition of substances to form free radicals at 77°K prove convincingly that the sensitisation of these processes takes place by a two-photon mechanism. It has been shown that the second quantum is absorbed by a triplet molecule of the aromatic compound, which acts as sensitiser. The least well-established feature is the final stage of the photoprocess—the mechanism of the interaction of the photoexcited sensitiser with the molecules undergoing photolysis. Three suggestions have been put forward regarding the type of interaction and the mechanism of the decomposition of the molecule undergoing photolysis to free radicals, recorded by the EPR method.

1. The formation of a complex of the charge-transfer type between a molecule of the sensitiser, photoexcited to a high triplet state, and a molecule of the dissociating substrate, followed by removal of a hydrogen atom [23,88,89,91] or decomposition with the formation of free-radical products [152].

2. Two-photon ionisation of the sensitiser molecule with subsequent dissociative attachment of an electron (solvated electron) to a molecule of the substrate [153,154].

3. Non-radiative transfer of energy from the photoexcited sensitiser to a molecule of the dissociating substrate with excitation of the latter to the decomposition state [120,135,136,140,142,155,156].

The first view is held by Bagdasar'yan [152], who suggested that photoexcited molecules of the sensitisers at 77°K can form complexes with the surrounding solvent molecules (substrate). These complexes, which are of the charge-transfer type but are formed only from excited molecules, have a short lifetime. Dissociation (predissociation) of this complex (reverse transfer of an electron to the substrate RH) may lead to decomposition of the solvent molecule (substrate) to free radicals. For example:



Gribova [23,88,89,91] proposed the following scheme for the two-photon dehydrogenation of ethanol by Mg etioporphyrin at 77°K. The chromophore molecule is converted into a lower triplet state under the influence of the first photon ($\lambda = 578$ nm). The second light quantum ($\lambda < 320$ nm), absorbed by the triplet molecules of the chromophore, transfers an electron of the triplet molecule of the chromophore to a state with higher energy. The strong coupling between the electrons forming the state of the chromophore with spin equal to 1 is weakened to such an extent that a labile biradical is produced (spin equal to 1/2). The chromophore molecule in this state is very active and adds on a hydrogen atom from neighbouring molecules of the matrix (ethanol), leading to the production of free radicals of dehydrogenated ethanol. Simultaneously, the Mg etieporphyrin molecule becomes a semi-reduced free radical. Study of the optical absorption spectrum of an irradiated frozen solution of Mg etioporphyrin in ethanol confirmed the formation of a free-radical form of the chromophore in this photochemical system.

Alfimov and coworkers [153] put forward yet another possible mechanism for the photosensitised dehydrogenation of alcohols by aromatic amines (diphenylamine or carbazole), involving two-photon ionisation of the amine molecules and interaction of the electrons produced with molecules of the alcohol. During the photodecolourisation of methanol solutions of diphenylamine and carbazole irradiated with ultraviolet light at 77°K, Alfimov and coworkers

found that the disappearance of the absorption band of the solvated electrons with λ_{max} = 600 nm is accompanied by a simultaneous increase in the concentration of alcohol radicals $\dot{C}H_2OH$. They therefore suggested that the formation of the $\dot{C}H_2OH$ radicals is associated with the disappearance of the centres absorbing light of λ = 600 nm, that is solvated electrons.

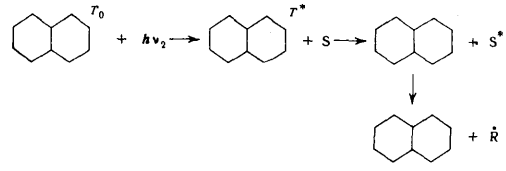
Shelimov and coworkers [154] tried to attribute the photosensitising action of aromatic hydrocarbons to the participation of ionic states formed by the action of ultraviolet light with short wavelength (λ < 300 nm) on their solutions in aliphatic hydrocarbons and alcohols at 77°K. For this purpose, they studied the decomposition of compounds with clearly defined electron-donating and electron-accepting properties in alcohol and hydrocarbons matrices, sensitised by aromatic hydrocarbons [154]. They carried out the photolysis of alcoholic solutions of naphthalene and phenanthrene in the presence of added compounds of the type R–Cl (n-propyl chloride, isopropyl chloride, benzyl chloride, methylene chloride, and carbon tetrachloride). In all instances with the exception of CCl_4, the formation of alkyl radicals $\dot{R}$ was observed. The rate of their formation was proportional to the square of the light intensity. If two-quantum photoionisation of naphthalene and phenanthrene [157] under the influence of ultraviolet light with λ = 254 nm is assumed, the formation of $\dot{R}$ radicals can be attributed to the dissociative attachment of an electron: $e + RCl \rightarrow \dot{R} + Cl^-$. The fact that the optical absorption spectra and the EPR spectra do not show the signals of the sensitiser radical-cations (A^+), which according to the photoreaction scheme should accumulate, was attributed by Shelimov to the disappearance of the greater part of these radical-cations by a "discharge" reaction: $A^+ + Cl^- \rightarrow A^* + \dot{C}l$. In the opinion of Shelimov and coworkers [154], the two-quantum formation of alcohol radicals during the illumination of solutions of aromatic compounds in ethanol at 77°K can also be explained by assuming photoionisation of the aromatic sensitisers followed by reaction of an electron with the oxonium ion ($CH_3CH_2OH_2^+$) or molecule of the alcohol ($CH_3–CH_2O^-H^+$). As confirmation of this suggestion, they give data on the observed increase in the rate of formation of alcohol radicals with decrease in the pH of the medium (increase in the concentration of $CH_3CH_2^+$ ions).

According to the suggestions which we put forward [120, 135,136,155], the final stage in the two-photon sensitisation of the rupture of the C_α–H and C–CH_3 bonds in alcohols and ethers and the C–I(Br, Cl) bonds in alkyl halides at 77°K involves the non-radiative transfer of energy from the photoexcited sensitiser in a high triplet state (aromatic amine, N-heterocycle, aromatic hydrocarbon, dye) to a molecule of the substrate (alcohol, ether, alkyl halide). We turned our attention [135,143,150] to the energetics of the photophysical stage of the two-photon sensitisation of the rupture of the C–I bond in alkyl iodides and the C–CH_3 bond in t-butyl alcohol at 77°K in the presence of aromatic compounds. It was found that the total energy of photoexcitation of the added sensitiser $E_{T_0} + h\nu_2$, where E_{T_0} is the energy height of the triplet level T_0 of the sensitiser, and $h\nu_2$ the photon absorbed by the sensitiser molecule in the triplet state, is always equal to or slightly greater than the energy of the photon $h\nu_{diss}$ bringing about the direct photodecomposition of the substrate molecules.

This energy relationship is a necessary condition for the non-radiative transfer of energy [158]. As a result of this resonance transfer of energy, the substrate molecule either is transferred directly to the repulsion potential curve of the bond being broken (C–H, C–CH_3, or C–I), which corresponds to excitation of a σ – or n-electron to a non-bonding orbital (σ–σ^* or n–σ^* transition) or decomposes by a predissociation mechanism. The efficiency of the transfer of energy to the substrate from the sensitiser photoexcited to a high triplet state is determined by the multiplicity of the electronic state of the substrate to which the energy is transferred [158–163]. The probability of energy transfer from an excited triplet level of the sensitiser (energy donor) to a triplet level of the substrate molecule (energy acceptor) should evidently be significantly greater than that for transfer to a singlet level, in accordance with the principle of preservation of the total spin of the system.

Since these intermolecular interactions have a limited sphere of influence [160–163], the dependence of the yield of radicals of the substrate on its concentration in a photochemically neutral matrix at 77°K at constant sensitiser concentration and constant experimental conditions, or, in principle, the magnitude of the radius of the sphere of influence of energy transfer, can be used to determine precisely the type of resonance energy transfer (triplet–triplet or triplet–singlet). We carried out these measurements [135,155] for two systems: naphthalene + t-butyl alcohol in ethanol and naphthalene + methyl iodide in ethanol at 77°K. The sphere of influence of the intramolecular energy transfer was taken as the averaged distance between the molecules of the energy donor and the energy acceptor, for which the probability of energy transfer from a molecule of the sensitiser (donor), excited to a high triplet state, to a molecule of the substrate (acceptor) was equal to the probability of intramolecular deactivation of the photoexcited sensitiser ($T^* \rightarrow T_0$ transition). The results showed that the characteristic radius of the sphere of interaction between the photoexcited sensitiser and the substrate is limited and is equal to 10–12 Å; this is characteristic of exchange-resonance interaction leading to triplet–triplet energy transfer [163].

Siegel and coworkers [142,143] reached a similar conclusion regarding the final stage of the mechanism of the two-photon sensitisation of the dehydrogenation of ethanol, diethyl ether, and methylcyclohexane, and also polydimethylsiloxane, by means of naphthalene. On the basis of their results they suggested that there is non-radiative resonance transfer of energy from a naphthalene molecule, photoexcited to a high triplet state, to a molecule of the solvent (ethanol, diethyl, or methylcyclohexane), followed by dissociation (rupture of the C–H bond). The proposed scheme for the two-photon sensitisation of the dehydrogenation of the solvent is as follows:



Douzou and coworkers [140] hold the same view regarding the mechanism of the two-photon sensitisation of the dehydrogenation of alcohols by aminoacids and nucleic acid bases.

Porter and coworkers [156] recently reproduced the experiments of Shelimov and coworkers on the two-photon sensitisation of dehydrogenation of unsaturated hydrocarbons by benzene derivatibes and various polycyclic compounds, and they also suggest that the final stage in

the sensitisation mechanism is the transfer of energy from the sensitiser, photoexcited to a high triplet state, to a molecule of the solvent (hydrocarbon), which is thus excited to a triplet decomposition state.

Since there is at present insufficient information for final resolution of the problem of the mechanism of the recently discovered two-quantum reactions of sensitised decomposition, it is necessary to carry out new and comprehensive studies in this direction by a combination of various physical methods of study (spectroscopy, EPR, mass spectroscopy, photoconductivity, etc.).

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Shpol'skii's Method in the Spectroscopy of Polyatomic Molecules

R.N.Nurmukhametov

This review examines various general historical aspects of Shpol'skii's method, together with the results obtained for various classes of organic compound; problems of the relationship between the form of the vibronic spectrum and molecular structure are considered, and various analytical applications of the procedure of quasi-line spectra are described briefly. The bibliography contains 161 references.

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1. SHPOL'SKII'S SPECTRA. FUTURE PROSPECTS IN RESEARCH AND ITS APPLICATIONS

A molecule is a quantum system with a discrete set of characteristic energy states, but the electronic spectra of molecules usually have the form of broad bands with little structure.

In practice we study the spectra not of a single isolated molecule, but of a large number of molecules undergoing greater or lesser external perturbation. It might seem that the spectra of vapours should be closest to the spectrum of an individual molecule, but the spectra of vapours of polyatomic molecules are generally extremely unsharp. Without going into all the reasons for the lack of sharpness in the structure of the electronic bands of vapours, we would merely mention as an obvious factor the "spreading" of the vibrational sublevels of the quasi-continuous system of rotational sublevels (due to the small magnitude of $\Delta E_{rot} \simeq 1\ cm^{-1}$). As a result of this and other factors, the unsharp structure cannot be resolved, irrespective of the resolving power of the instrument. It should also be mentioned that many compounds are unstable in the vapour state.

Aromatic polyatomic molecules are usually studied in the condensed phase, in the form of liquid and solid solutions, or pure and mixed crystals. The best spectral resolution in the condensed phase is obtained at low temperatures for crystals and solid solutions. Molecular rotation is restricted at low temperature. Moreover, nonradiative processes are suppressed at low temperatures, leading to an intensification of fluorescence and the appearance of the intercombinationally forbidden $T-S_0$ emission—phosphorescence. For a long time it was assumed that the intramolecular factors leading to loss of sharpness in the structure were the principal factors, so that it was assumed to be impossible to improve the resolution of the structure by altering the molecular environment.

In 1952, Shpol'skii and coworkers[1] obtained the quasi-line spectra of a number of complex aromatic molecules in frozen crystalline solutions. The discovery of the quasi-line spectra of polyatomic molecules stimulated a large number of new studies in the field of the electronic spectroscopy of complex organic compounds. The investigation of the origin of the electronic spectrum of a molecule involves two types of problem: 1) the determination of the frequency of the electronic transition, and its interpretation; and 2) the determination of the mechanism of formation of the band contours, that is the interpretation of its vibrational structure. Problems of the first type were solved with some approximation from spectra with broad bands, but the solution of problems of the second type could be solved only by resolving the structure of the bands. Quasi-line spectra are very characteristic, and they can be used to determine with high accuracy the frequency and intensity of the purely electronic band and the vibrational frequencies combining with the given electronic transition. These spectra reflect more deeply the characteristic features of the electronic and spatial structures of a molecule (this is examined in detail in section 3). Examination of the dependence of the vibronic spectra on structure can be used to find possible answers to the following questions: why is the observed system of electronic bands characteristic of the molecule, what is the mechanism of formation of the bands (the vibrational structure), and what contribution do the various atomic groups constituting the molecule make to its electronic state? The form of the vibrational structure and its degree of resolution are closely related to the nature of the electronic transition, so that the structure can give definite information on the nature of the transition responsible for the electronic band being considered. On the other hand, if we know the relationship between the nature of a transition and the structure of the band, it is possible to predict beforehand the expected form of the vibrational structure and the changes which it undergoes with change in the nature of the electronic transition, which in turn may be changed by definite changes in the structure of the molecule.

The manifestation of the frequency ranges representing a combination or overtone of the normal vibrations makes it possible to examine the problems of the interaction of vibrations and the form of the potential surface. In particular, the decrease in the frequency range in the overtones relative to the additive sum establishes the degree of anharmonicity of the potential curve. The interpretation of the vibrational structure makes it possible to determine which vibrations are involved in the most effective conversion of the electronic excitation energy into vibrational energy. Quasi-line absorption spectra reveal the frequencies of the vibrations of molecules in electronically excited states. Thus the examination of these spectra provides a simple method for determining the vibrational frequencies of excited molecules.

At first, the range of molecules studied was restricted to aromatic polycyclic condensed hydrocarbons. These molecules have a rigid planar structure, and this facilitates

resolution of the vibrational structure of the bands, which, moreover, are determined in the near ultraviolet and visible ranges by the same type of $\pi-\pi^*$ transition. It was not clear whether it was possible to obtain a quasi-line spectrum for molecules containing heteroatoms. In 1958, Shigorin and coworkers[2] reported the quasi-line luminescence spectrum of anthraquinone and its derivatives. Subsequently, Shpol'skii's method was successfuly extended to the molecules of compounds of various classes. A quasi-line structure was not always obtained, particularly for molecules with a non-rigid structure, but a sufficiently clearly resolved vibrational structure, suitable for analysis, was often attained. From the degree of resolution, in turn, it was possible to obtain information on the intramolecular factors leading to loss of sharpness of the bands, and on the spatial structure of the molecules. The stabilisation of certain radicals in solid matrices at low temperatures makes it possible to obtain Shpol'skii's quasi-line spectra not only for molecules, but also for radicals (see R.p. 355).

A large number of studies have been devoted to the vibronic spectra of aromatic molecules, with a chain structure, widely used as scintillating additives (polyphenyls, diphenylpolyenes, arylethylenes, aryloxadiazoles, diarildivinylbenzenes, arylnaphthoxazoles, benzoxazoles, etc.). Shpol'skii's method has been used to study the spectra of aromatic aldehydes, ketones, diketones, various dyes and related compounds (xanthone, acridones, phthalimides, thioindigoids, and indigoids), and *N*-heteroaromatic molecules (the aza-heteroanalogues of triphenylene, quinoline, and bipyridyls). Finally, a quasi-line structure has been obtained for the spectra of the complex molecules of phthalocyanines and porphyrins.

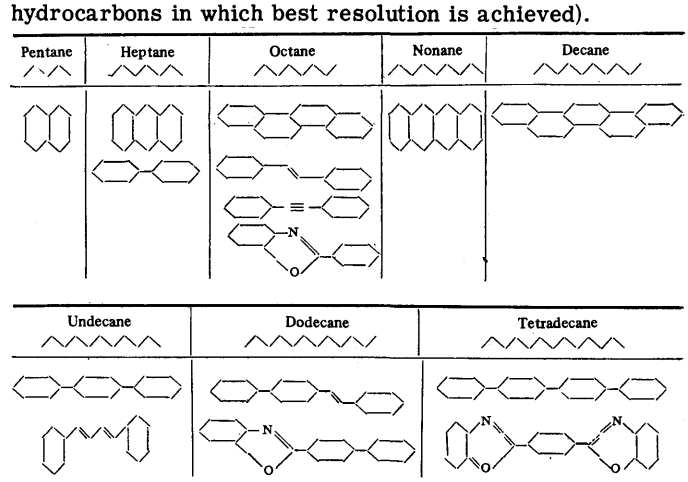
To obtain quasi-line spectra, Shpol'skii and coworkers used a comparatively simple procedure, which can be described briefly as follows: 1) highly dilute solutions with concentrations of $10^{-4}-10^{-5}$ M are used, so that there is almost no interaction between the dissolved molecules; 2) inert neutral solvents—saturated n-hydrocarbons—are used as media; 3) the solutions are cooled to low temperature (77, 20, and 4 °K) and are frozen to form a crystalline mass; and 4) the spectra of these frozen solutions are studied.

By the use of mixed solvents, Shpol'skii's method was extended to compounds which do not dissolve directly in n-hydrocarbons. Thus the spectra of phthalocyanines was obtained with a solution in acetone[3], which was then diluted with n-hydrocarbons. When a benzene solution of perylene was diluted with hexane, the spectrum obtained did not differ from the spectrum of the pure hexane solution[4]. Indigo and indigoids were dissolved in hexane by means of a dioxan solution[5]. A similar technique was used to obtain the spectra of *N*-substituted acridones[6,7].

The range of matrices in which a quasi-line structure can be obtained has been extended. Sponer, Kanda, and coworkers[8-10] showed that these spectra are also obtained in a cyclohexane matrix. Sheremet'ev and Val'dman[11] obtained the quasi-line spectrum of perylene in dibenzylaminoethanol. We showed for the example of pyrene in poly-2-methylpropene[12,13] that it is possible to resolve a quasi-line structure in a polymeric matrix. It has been reported[4] that the spectra of pyrene show a quasi-line structure in hexanol at 77 °K.

A remarkable characteristic feature of quasi-line spectra is the frequently observed multiplet structure of the vibronic bands, so that the spectrum consists of the superposition of several identical molecular spectra, displaced relative to one another. The degree of resolution and the multiplet structure of the bands are found to be very characteristic of the solute–solvent system. Analysis of the characteristic features of quasi-line spectra established one important reason for the loss of sharpness in the spectra of solid solutions—non-uniform perturbation of the electronic levels of the dissolved molecules by the field of the environment (as a result of non-uniformity of the matrix) leading to dispersion of the energies (frequencies) of the electronic transitions in the set of molecules. Experiment shows that it is possible to eliminate this dispersion by choice of a suitable solvent. Although there is no general rule for the selection of a solvent in which we can expect the best resolution of the structure for a given compound, in some instances it is possible to use a relationship established by Bolotnikova[14-16], who showed that the best resolution of the spectra of polyacenes is observed in those hydrocarbons whose molecular dimensions are close to those of the polyacene. Thus the best resolution was obtained in pentane for naphthalene, in heptane for anthracene, and in nonane for naphthacene (Table 1). A similar result was obtained for the angular hydrocarbons chrysene[17], picene[18], and benzanthracene[19]. Gobov[20,21] showed that this rule is applicable for the biphenyl–terphenyl–quaterphenyl series, for the diphenylpolyenes stilbene and diphenylbutadiene, and for various benzoxazoles[22] (see Table 1). It is not a universal rule, however. As

Table 1. The role of correspondence in the dimensions of the molecules of the solvent and the luminophor in improving the resolution of the vibrational structure of electronic bands. The upper row gives the carbon frameworks of the n-hydrocarbon molecules, and the lower row gives the frameworks of the luminophor molecules (under the n-hydrocarbons in which best resolution is achieved).



an illustration, we would point out that the spectrum of 1,4-distyrylbenzene, whose molecule is longer, by the length of the styryl group, than that of stilbene, is most clearly defined in hexane[23], and not in n-hydrocarbons with a longer chain. The high sensitivity of the structure to the solvent, concentration, and method of freezing, and in some instances to the presence of impurities, provides an effective indicator for the study of the fine effects of intermolecular interaction.

We shall not consider in detail experimental data on the investigation of the nature of the multiplet structure[24-26]; these are discussed in detail in reviews by Shpol'skii[4,27-30]. The aim of the present review is to examine the progress made in the study and interpretation of the vibronic spectra of molecules of various classes, and the new information which has been obtained on the relationship between electronic spectra and structure (the manifestation, in the spectra, of the characteristic features of the electronic transition and the electronic and spatial structures of the molecules, particularly in the excited state). A quasi-line structure cannot be obtained for all molecules. In the present review an attempt is made to determine which factors of the intramolecular structure influence the resolution (or lack of resolution) of the structure.

The high sensitivity and characteristic nature of quasi-line spectra have provided a basis for a number of spectroscopic-analytical methods for the qualitative and quantitative determination of substances in various products. These problems will be examined in section 4.

2. THE QUASI-LINE SPECTRA OF VARIOUS CLASSES OF COMPOUND

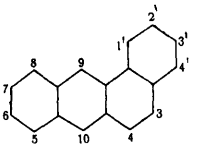
Aromatic polycyclic condensed hydrocarbons. The compounds of this class which have been studied by Shpol'skii's method are given in Table 2; for all of these, a quasi-line structure has been obtained in a suitable solvent. A general characteristic feature of the vibrational structure of the electronic bands for compounds of this class is that the frequencies of the normal vibrations of the carbon framework predominate. The vibrational frequencies active in the luminescence spectra correspond to the vibrations of the molecule in the ground electronic state and are equal to or very close to the frequencies active in the Raman spectrum of the same compound. Another characteristic feature of the structure of the electronic bands of aromatic hydrocarbons is the appearance of common frequencies with very similar values. An analogous picture of very similar frequencies is observed in the infrared spectra of various aromatic hydrocarbons, so that the spectra are not characteristic, and are unsuitable for analytical purposes. We shall not deal in detail with the problems of the relationship between the vibronic spectra and the structure of molecules of this class, since this has already been done[62].

Table 2. Aromatic condensed hydrocarbons with quasi-line spectra which have been studied.

Compound	References	Compound	References
Benzene	8,31,32	1,2,4,5-Dibenzpyrene	48
Naphthalene	15,33-35	3,4-Naphtho-6,7-benzpyrene	47
Anthracene	14,16,36,37	3,4,8,9-Dibenzpyrene	48
Naphthacene	14,16,37	1,12-Benzperylene	49,50
Phenanthrene	38-41	Perylene	51-53
Benzanthracene	19	Triphenylene	54,55
Chrysene	17	Fluoranthene	56
Dibenzanthracene	14	Fluorene	8,57,58
Pyrene	14,42,43	Acenaphthene	58,59
1,2-Benzpyrene	44	Rubicene	60
3,4-Benzpyrene	45	Azulene	61
Picene	18,46	Pentacene	46
Penthaphene	46	Benznaphthalene	46

Aromatic hydrocarbon radicals. Grajcar and Leach[63] obtained absorption spectra ($\nu_{0-0} = 21\,580\,cm^{-1}$) and fluorescence spectra ($\nu_{0-0} = 21\,630\,cm^{-1}$) showing considerable structure for the benzyl radical at 77°K in a methylcyclohexane + 3-methylpentane (2:3) matrix. The fluorescence spectra showed vibrational frequencies of 570, 965, 1050, 1295, and 1460 cm^{-1}, some of which are close to the vibrational frequencies of benzene. Ripoche[64] studied the fluorescence spectra at 88°K for benzyl radicals, again produced by the photolysis of toluene, in new matrices—cyclopentane, methylcyclopentane, and methylcyclohexane. Under these conditions he obtained quasi-line spectra with a large number of quasi-lines; he made a detailed vibrational analysis and assigned the frequencies to definite types of normal vibration. Vibrational frequencies were distinguished at 363, 532, 820, 872, 982, 1017, 1087, 1145, 1376, 1439, 1475, 1540, and 1593 cm^{-1} (in cyclopentane). Mileshina and coworkers[65] obtained the quasi-line fluorescence spectrum of the diphenylmethylene biradical in a hexane matrix at 77°K. This spectrum is due to a $T^* \rightarrow T_0$ transition (the ground state of diphenylmethylene is a triplet state) and is interpreted by means of the frequencies 630, 800, 1012, 1170, and 1600 cm^{-1}, which are close to the vibrational frequencies of the benzene ring, active in the fluorescence spectra of the benzyl and triphenylmethyl radicals.

Substituted aromatic hydrocarbons. The introduction of substituents influences the electronic structure, electronic transitions, symmetry, and spatial configuration of the molecule, and alters its dimensions and the nature of its interaction with solvent molecules. All this is reflected not only in the position and intensity of the electronic bands, but also in the nature of the vibrational structure and its degree of resolution. Let us consider first the spectra of alkyl, halogeno, and vinyl derivatives of aromatic hydrocarbons. Kharitonova[66] studied the quasi-line spectra of α- and β-methylnaphthalenes in hexane at 20°K. Dikun[67,68] obtained the quasi-line spectra of ~ 40 derivatives of 1,2-benzanthracene with alkyl and halogeno substituents.



Fenina[19,69] carried out a more detailed study and interpretation of the vibrational structure of the fluorescence spectra of 1,2-benzanthracene and all its monomethyl derivatives, and from the quasi-line spectra determined the frequencies of the long-wave ^1L_b–$^1A_1$ transition. The maximal long-wave displacement (450 cm^{-1}) was observed when the CH_3 group was introduced into position 9 or 10, a marked displacement was observed for the 3-methyl derivative (300 cm^{-1}), approximately equal medium displacements of 100 cm^{-1} were observed for substitution in the 1'-, 2'-, 4'-, and 7-positions, a small displacement was observed for the 3'-, 5-, 8-, and 4-CH_3 derivatives, and 6-CH_3-benzanthracene even showed a slight short-wave displacement. The values of the displacements only in a few instances agree with the predictions of the theory of the influence of alkyl substituents on the energy of the electronic transitions of benzanthracene. On the basis of an analysis of the quasi-line absorption spectra it was concluded that the frequency of the ^1L_a–$^1A_1$ transition in benzanthracene is 1600–1700 cm^{-1} higher than the frequency of the ^1L_b–$^1A_1$ transition. The spectra of all the derivatives

except the 3-methyl derivative were sharper in octane. The spectra of the 3-methyl derivative are equally sharp in hexane and heptane, and less sharp in octane.. The sterically hindered substituents in positions 9 and 1′ produce a marked decrease in the sharpness of the structure. Utkina [70-72] made a systematic study of anthracene derivatives, and showed that the introduction of alkyl substituents (methyl, ethyl, and propyl) lowers the frequency of the electronic transition by about 700–750 cm^{-1}, and the introduction of two alkyl substituents produces a displacement which is approximately twice this value. The attachment of an allyl radical with the $-CH=CH_2$ double bond isolated from the π system of the anthracene nucleus produces the same displacement of the spectra as alkyl radicals. When the double bond is conjugated (in 9-vinylanthracene), however, the long-wave displacement of the band amounts to about 2000 cm^{-1}, that is by an amount characteristic of an increase in the π system by a double bond in the direction of the electronic transition being considered. The structure of the fluorescence spectrum is less sharp, the greater the steric hindrance in the molecule. A particularly marked decrease in sharpness is observed as a result of the introduction of vinyl groups. The phenanthrene derivative retene gave a quasi-line structure very similar to the structure of the spectra of the unsubstituted molecule. A quasi-line structure was also obtained for halogenopyrenes. The introduction of halogens improves the resolution of the structure considerably. Val'dman [11] obtained a quasi-line fluorescence spectrum for a complex derivative of perylene—di-isobutyl perylene-3,9-dicarboxylate. Hydrocarbon derivatives containing the electron-donating groups NR_2, NR, OR, and SR (aromatic amines, ethers, and thioethers) will be examined below.

N-Heteroanalogues of aromatic hydrocarbons have been studied by Shpol'skii's method to a much smaller extent, apparently due to the difficulties encountered in the resolution of their structure. In the first place, many of these compounds either do not show fluorescence, or show only weak fluorescence in non-polar solvents, because of strong deactivation due to singlet–triplet conversion with the participation of excited $n-\pi^*$ states [73-76]. Secondly, thanks to the presence of the n electrons of the N atom, these molecules readily undergo association with polar molecules, traces of which are almost always present in hydrocarbon solvents.

Mamedov described the quasi-line phosphorescence spectra of quinoline in hexane [77] and pentane [78] and of 5,6-benzquinoline in hexane [78]. Ruziewicz [79,80] resolved the structure of the phosphorescence bands of 1,4-diazotriphenylene and 1-azotriphenylene. El-Sayed [81] reported the quasi-line structure of the luminescence band of pyridazine in hexane.

Polyphenyls and diphenylpolyenes. Gobov [20,21,82-84] described the structure of the luminescence spectra of biphenyl, terphenyl, and quaterphenyl at 77 °K, and showed that the best resolution of the structure for the longer polyphenyl molecules is obtained in the hydrocarbons with longer chains: in hexane and heptane for biphenyl, in undecane for terphenyl, and in cetane ($C_{15}H_{30}$) for quaterphenyl. The fluorescence band of the O–O transition has a frequency of 33 355 cm^{-1} in biphenyl, and lower values of 30 715 cm^{-1} in terphenyl and 28 080 cm^{-1} in quaterphenyl, that is the frequency is reduced by about 2600 cm^{-1} with increase in the size of the molecule by one phenyl unit. A common characteristic of the structures of the fluorescence spectra of polyphenyls is the predominance of the frequency of the antisymmetric pulsating vibration of the benzene ring at 1600 cm^{-1}. In the spectra of terphenyl and quaterphenyl it forms intense progressions, determining the periodic form of the structure. The range of their fluorescence bands is determined by the overtones 4×1600 cm^{-1}. Biphenyl gives a structured phosphorescence band with $\nu_{0-0} = 22\,905$ cm^{-1}; visible phosphorescence is not observed for terphenyl and quaterphenyl.

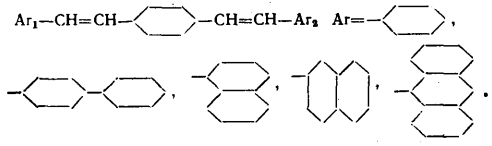
As early as 1935, Hausser and coworkers [85] made a systematic study of the absorption and luminescence spectra of a series of diphenylpolyenes with $n = 1-7$. They observed a regular displacement of the spectra towards longer wavelengths with increase in the number of polyene groups in the molecule. The structures of the fluorescence spectra of diphenylpolyenes are very similar and are described by a series formula $\nu = \nu_0 - 1550\,n_1 - 1660\,n_2$, where $n_1 = 0.1$, $n_2 = 2.3$, and ν_0 has values 29 730 cm^{-1} for stilbene ($n = 1$), 27 250 cm^{-1} for diphenylbutadiene ($n = 2$), 24 900 cm^{-1} for diphenylhexatriene ($n = 3$), 22 135 cm^{-1} for $n = 4$, and 19 870 cm^{-1} for $n = 5$. The vibrational structure of the spectra of stilbene was subsequently studied many times. Gobov [83] and Levshin and Mamedov [86] resolved the vibrational structure of the fluorescence band and the long-wave absorption at 77 °K in octane. Malykhina and Shpak [87] studied the quasi-line spectra in polarised light for an octane–stilbene single crystal, and Dyck and McClure [88] made a similar study of a bibenzyl–stilbene single crystal. The frequency of the $S_1^*-S_0$ transition for stilbene is 30 034 cm^{-1} in octane and 29 903 cm^{-1} in bibenzyl. All the authors cited showed that the form of the spectrum is determined chiefly by the progressions of the frequency of the stretching vibration of the ethylene group ($\nu_{C=C}$ = 1640–1659 cm^{-1} in fluorescence, and 1600 cm^{-1} in absorption). The spectrum also shows another seven frequencies, observed independently and in combination with the above frequency; most of these seven frequencies are assigned to the skeletal vibrations of the benzene rings.

The structured fluorescence spectra of stilbene, diphenylbutadiene, and diphenylhexatriene show considerable resemblances to the spectra of polyphenyls. Their structure has a similar periodic form, determined by the progressions of the frequency of the stretching vibration of the ethylene and polyene groups. This frequency lies at 1640 cm^{-1} in stilbene, 1616 cm^{-1} in diphenylbutadiene, and 1600 cm^{-1} in diphenylhexatriene (for the latter, only a coarse vibrational structure is observed; the spectrum [89] consists of broad bands with $\Delta\nu \simeq 400$ cm^{-1}). The band for the O–O transition in stilbene (30 034 cm^{-1}) is very close to the band for terphenyl (30 715 cm^{-1}), and the band for diphenylbutadiene (27 948 cm^{-1}) is very close to the band for quaterphenyl (28 080 cm^{-1}), so that the replacement of the internal phenyl units in the polyphenyl chain by an ethylenic bond does not alter significantly the position of the absorption and fluorescence bands of this chain π system. This is true, however, only for the initial members of the polyphenyl series; with further increase in the length of the polyphenyl chain, the decrease in the frequency of the long-wave transition is much smaller than that for increase in the length of the polyene chain in diphenylpolyenes [90].

Arylethylenes. Fluorescence spectra of arylethylenes in n-hydrocarbons at 77 °K, with the most clearly defined structures, were obtained [89,91] for phenylstilbene in undecane and dodecane, and for di-α-naphthylethylene, di-β-naphthylethylene, α-naphthyl-β-naphthylethylene, and β-naphthylphenylethylene in hexane. The fluorescence

spectrum of diphenylstilbene in all n-hydrocarbons can be resolved only into broad bands ($\Delta\nu \simeq 300$ cm^{-1}). Decrease in temperature to 20°K did not lead to additional resolution of the structure of the spectrum of phenylstilbene; only a slight decrease in the width of the bands was observed[89]. A characteristic common feature of the vibronic spectra of arylethylenes is the periodic form of the structure. The period interval is a frequency in the range 1600–1640 cm^{-1}, assigned to the stretching vibration of the ethylenic bond. The frequency decreases with increase in the weight of the aryl radicals and with increase in the efficiency of the conjugation (estimated from the decrease in the frequency of the electronic transition). In the fluorescence spectra it has the value 1640 cm^{-1} for stilbene, 1635 cm^{-1} for β-naphthylphenylethylene, 1620 cm^{-1} for phenylstilbene, 1610 cm^{-1} for α-naphthyl-β-naphthylethylene, and 1600 cm^{-1} for di-α-naphthylethylene. The width of the fluorescence band for these molecules is determined by the range 4×1600 cm^{-1}, and the maxima in the fluorescence spectrum at room temperature are separated from one another by about 1600 cm^{-1}.

Diaryldivinylbenzenes



The fluorescence spectra have been studied[23] at 77°K in hexane, heptane, octane, nonane, undecane, and heptadecane solutions. A well resolved vibrational structure was obtained for most compounds. The narrowest bands were obtained for solutions of distyrylbenzene and di-β-naphthyldivinylbenzene in hexane. The bands in the fluorescence spectra of bis(biphenyl)-, di-β-naphthyl, β-naphthylphenyl-, α-naphthylphenyl-, and biphenylphenyldivinylbenzenes were found to be more diffuse, but the fluorescence spectrum of dianthryldivinylbenzene has very narrow bands. The poor resolution of the structure for the latter compounds is due to the appreciably non-planar structure of the molecule, resulting from considerable steric hindrance. A common characteristic feature of the structured spectra of diaryldivinylbenzenes is the periodic form of the structure, in which the frequencies of the range 1550–1520 cm^{-1}, corresponding to the stretching vibrations of the divinylbenzene group and its overtones, predominate.

Arylacetylenes. Gobov[83] described the structure of the luminescence and absorption spectra of tolane in n-octane. The fluorescence spectrum was interpreted by means of the frequencies 260, 524, 700, 1000, 1150, 1493, 1600, and 2232 cm^{-1}; the same frequencies, with the exception of 524 cm^{-1} and 1493 cm^{-1}, were distinguished in phosphorescence. The 2232 cm^{-1} frequency, which is the most characteristic of the spectrum and combines with the other frequencies, shows appreciable anharmonicity and is assigned to the stretching vibration of the acetylenic group. In the absorption spectrum the frequency is lowered to 2150 cm^{-1}. The 1000 cm^{-1} and 1600 cm^{-1} frequencies were interpreted as characteristic frequencies of the benzene rings.

The structures of the long-wave absorption, fluorescence, and phosphorescence spectra of phenylacetylene have been described[92]. The triple bond vibrational frequency, whose value is lowered to 2100 cm^{-1} as a result of kinematic factors, is also active in the luminescence spectra. This frequency, however, does not predominate in the spectrum, and the frequencies of the benzene ring, particularly the 1600 cm^{-1} and 1000 cm^{-1} frequencies, are equally active. In agreement with the low intensity of the long-wave absorption band, a relatively low intensity is observed for the O–O band, indicating an electronic transition partly forbidden by symmetry. The superposition of the incompletely symmetrical vibration at 600 cm^{-1} partly removes the forbidden character. This is characteristic of benzene derivatives such as phenylacetylene, styrene, biphenyl, and naphthalene. The transition is not forbidden in phosphorescence. Phenylacetylene and tolane are characterised by a difference in the $S_1^* - T$ splitting of 10 000 cm^{-1}, which is the same as that in the polyacene series. Bagratishvili and coworkers[93] obtained the quasi-line fluorescence and phosphorescence spectra of bi-β-naphthyl, whose molecule is appreciably non-planar due to steric hindrance. The band structure contains many "naphthalene" frequencies.

Benzoxazoles and naphthoxazoles. The quasi-line fluorescence spectra of 2-phenylbenzoxazole, 2-biphenylylbenzoxazole, 2-styrylbenzoxazole, 1,4-di-(2′-benzoxazolyl)-benzene, and 1,4-di-(2′-benzoxazolyl)-ethylene in n-hydrocarbon solutions at 77°K have been described and interpreted[22]. It was shown that the fluorescence spectrum is determined by the $\pi-\pi^*$ transition, and that the π system of these molecules is isoelectric with the π system of the corresponding arylethylenes, for example the phenylbenzoxazole and stilbene molecules are π isoelectronic. The interaction of the unshared pairs of electrons of the O and N heteroatoms appears to lead to mutual exclusion of their influence on the π electronic system. The similarity in the π electronic structures leads not only to similar electronic bands and identical luminescence and scintillation properties, but also to an identical mechanism of formation of the vibrational structure of the bands. The structure of the spectra is characterised by a periodicity. The period corresponds to the stretching vibrations of the internal connecting group. In the phenylbenzoxazole molecule this is the C–N bond of the oxazole ring, and the predominant frequencies in the structure are those at 920, 1550, and 1610 cm^{-1}, which, according to the interpretation of the vibrational spectra[94] are the characteristic vibrations of the oxazole ring. In the molecules of 2-biphenylylbenzoxazole and 1,4-di-(2′benzoxazolyl)-benzene, the internal connecting group consists of a C=N bond and a phenyl ring; in the structure of the spectrum, the 1600 cm^{-1} vibrational frequency of the phenyl ring is correspondingly more active. In the molecules of 2-styrylbenzoxazole and 1,4-di-(2′-benzoxazolyl)-ethylene, this frequency is replaced by the vibrational frequency of the ethylenic group at 1640 cm^{-1}. The structures of the absorption spectra of these compounds have been obtained and analysed[95]. Very clearly defined structures were observed for the vibronic fluorescence and absorption spectra[96] of phenylnaphthoxazoles; the biphenylylnaphthoxazoles showed a less clearly defined structure. Their electronic bands were found to be similar to the bands of the corresponding naphthylphenylethylenes and biphenylnaphthylethylenes.

Aromatic amines, alcohols, and ethers. The electronic long-wave absorption and luminescence bands of amino- and *N*-dialkylamino-derivatives of aromatic hydrocarbons in solution at room temperature have the form of broad structureless bands. In vitreous solutions at low temperature, these are resolved into a number of comparatively broad bands. Ermolaev[97] described fluorescence and phosphorescence spectra of this type, with a

coarse vibrational structure, for a number of aromatic amines in EPA solutions (petroleum ether + ethanol + 3-methylbutane) at 77°K. For those compounds in which the amino-group is not included in the rigid framework and is capable of rotating relative to the C–N axis (for example in aniline, dimethylaniline, diphenylamine, and triphenylamine), it is not possible to observe greater resolution of the structure in n-hydrocarbon solutions compared with vitreous solutions. When the amino-group is rigidly fixed in the molecule, however, a quasi-line structure can be obtained. The spectra of carbazole in hexane and heptane have been obtained[98], and the quasi-line spectra of acridan have been described[7]. The fluorescence and phosphorescence spectra of these molecules show purely electronic bands of high intensity, indicating that the transitions are allowed. The skeletal vibrations, particularly that of the benzene ring at 1600 cm^{-1}, are active in the structure. Attempts to obtain an effectively resolved structure for the electronic bands of aromatic alcohols and ethers, such as phenol, naphthols, anisole, methoxynaphthalenes, etc. in n-hydrocarbon solutions did not give positive results. When the –O– or –S– bridge is part of a rigidly fixed structure, quasi-line spectra can be obtained (diphenylene oxide and diphenylene sulphide)[98]. The quasi-line fluorescence and phosphorescence spectra of diphenylene oxide have been described[100]. The quasi-line spectra of diphenylene oxide and carbazole have been studied[99,100].

Aldehydes and ketones. The luminescence spectra of aliphatic aldehydes—formaldehyde, acetaldehyde, propionaldehyde, and butyraldehyde—and ketones—acetone, diethyl ketone, methyl ethyl ketone, cyclohexanone, cyclopentanone, and cycloheptanone—in the vapour state and in n-hydrocarbon solutions frozen at 77°K have been studied[101]. Emission bands with little structure were observed in the vapours and solutions; slight improvement in the structure in solutions was observed for the aldehydes on going from butyraldehyde to acetaldehyde. The emission was attributed to the $T_{n-\pi^*}-S_0$ transition. The $n-\pi^*$ phosphorescence and long-wave $n-\pi^*$ absorption spectra of aromatic aldehydes and ketones (benzaldehyde, acetophenone, benzophenone, and their derivatives) are resolved in n-hydrocarbons at 77°K to give a few broad bands, as in the vitreous solutions[102,103]. The only frequencies which can be clearly distinguished in their structure are those of the stretching vibration of the C=O group, which form an intense progression. In the phosphorescence bands this frequency has the value 1680–1660 cm^{-1}, corresponding to the vibration in the ground electronic state, but in the absorption bands it is lowered to 1200 cm^{-1}, indicating a considerable decrease in the strength of the C=O bond in the excited $n-\pi^*$ state. In this state there is also a significant increase in the equilibrium distance in the C=O group, and this determines the nature of the distribution of the band intensities. When the keto-group forms part of a rigid structure, a quasi-line structure can be observed for the $n-\pi^*$ phosphorescence. Shigorin and Shcheglova[104] reported the quasi-line phosphorescence spectrum of anthrone, and we reported that of anthraquinone[2,25]. A detailed analysis of the quasi-line structure of the $n-\pi^*$ phosphorescence spectrum of anthraquinone was carried out[25]. It was shown that the $\nu_{C=O}$ frequency forms predominant progressions and combines with all other vibrational frequencies active in the spectrum. In aromatic aldehydes and ketones with $\pi-\pi^*$ phosphorescence, it is possible to obtain a quasi-line structure for its band, as shown for the example of biphenylaldehyde and α- and β-naphthaldehydes[105].

Derivatives of anthraquinone and other quinones. Shigorin and coworkers[106-111] studied the influence of the intramolecular interaction of various atomic groups in these compounds on the quasi-line luminescence and long-wave absorption spectra. It was shown that the introduction of various β-substituents (β-halogeno[2,25], β-carboxy, β-carbalkoxy[106], and β-alkyl[107]) into the anthraquinone molecule does not alter the nature of the luminescence band. The luminescence spectra of β-substituted anthraquinones are determined by the $n-\pi^*$ phosphorescence and exhibit a vibrational structure similar to that of the spectrum of anthraquinone, in which a progression of the vibrational frequency of the CO group of the anthraquinone ring predominates. The β-substituents produce only a slight change in the position of the spectrum and the multiplicity of its bands. The introduction of α-substituents (α-alkyl, α-aryl[107], and α-halogeno[108]) leads to a marked long-wave displacement of the absorption bands and to the appearance of a fluorescence band, often with an indistinct structure. Particularly marked changes are produced by α-hydroxy substituents and their ethers[111]. For the former, this can be attributed to the production of a stable intramolecular hydrogen bond with the formation of a quasi-aromatic ring. The formation of a ring of this kind has been assumed to be responsible for the production of a quasi-line structure in the absorption and fluorescence spectra of 1,4-dihydroxyanthraquinone and 1,2,5,8- and 1,4,5,8-tetrahydroxyanthraquinones, which are displaced considerably towards longer wavelengths compared with the spectra of anthraquinone. The influence of the nature and position of the substituent on the structure of the spectra for a series of naphthoquinone derivatives has been studied[110], and the dependence of the spectra of quinones on the number and relative arrangement of the keto-groups in the aromatic ring (anthrone, phenanthrenequinone, and anthraquinone) has been investigated[104].

Esters of dicarboxylic acids. Ivanova[111] recorded the structure of the fluorescence spectra of two diethyl esters of ω,ω′-dicarboxylic acids. Distinct resolution of the structure of the spectrum of $C_2H_5OOC.(CH=CH)_6COOC_2H_5$ was observed in n-octadecanol (half-width of the bands about 30–50 cm^{-1}), with initial ν_{0-0} band at 20023 cm^{-1}. The fluorescence bands of the ester $C_2H_5COO(CH=CH)COOC_2H_5$ were found to be more diffuse ($\Delta\nu \simeq 150$ cm^{-1}) and approximately the same in dodecane, cetane, and octadecanol. The most characteristic frequencies in the structure of the spectra were 1550 cm^{-1} and 1140 cm^{-1}, assigned to the stretching vibrations of the polyene chain. The long-wave absorption and fluorescence bands are determined in these esters by a $\pi-\pi^*$ transition, so that the characteristic frequencies of the carboxyl group do not appear distinctly in the structure.

Xanthone and acridones. The xanthone molecule contains two oxygen atoms joined in different ways to the π system, and the interaction of these atoms is responsible for a number of remarkable characteristic features. Under the influence of the electron-donating –O– bridge, the energies of the $n-\pi^*$ transitions are increased, and the energies of the $\pi-\pi^*$ transitions are decreased, so that the $n-\pi^*$ absorption band is partly overlapped by the $\pi-\pi^*$ band, although it remains a long-wave band, and the $T_{n-\pi^*}$ and $T_{\pi-\pi^*}$ levels have very similar energies, so that inversion of the positions of the $T_{n-\pi^*}$ and $T_{\pi-\pi^*}$ levels is observed[112] under the influence of solvent. In n-hydrocarbon solutions, xanthone exhibits short-lived $n-\pi^*$ phosphorescence, and in alcohol it exhibits long-lived $\pi-\pi^*$

phosphorescence. In hexane and heptance solutions at 77°K a quasi-line structure was obtained for the $n-\pi^*$ phosphorescence bands and two absorption bands, associated with the $\pi-\pi^*$ transitions ($\nu_{S_2^*-S_0}$ = 29 575 cm^{-1} and $\nu_{S_3^*-S_0}$ = 35 370 cm^{-1}). Under the same conditions, however, the $n-\pi^*$ absorption band remains diffuse. This makes it possible to define more precisely one of Kasha's distinguishing criteria for $n-\pi^*$ and $\pi-\pi^*$ bands, which says that in a condensed phase the $n-\pi^*$ bands are diffuse, whereas the $\pi-\pi^*$ bands have more structure. The example of xanthone shows that this is true only for the $n-\pi^*$ absorption bands, but not for $n-\pi^*$ phosphorescence.

The vibrational structure of the phosphorescence spectrum of xanthone has a very characteristic periodic form, determined by the fact that the $\nu_{C=O}$ frequency forms intense progressions and combines with all other vibrational frequencies. The values of the frequencies decrease in the overtones, indicating anharmonicity of the vibration of the C=O group. In the $\pi-\pi^*$ absorption bands, this predominance of one of the frequencies, which would be close to the frequency of vibration of the C=O group, is not observed.

In the acridone molecule the –NH– bridge is a stronger electron-donating substituent, so that the lower excited S_1^* and T levels are $\pi-\pi^*$ levels. Acridone itself does not dissolve in n-hydrocarbons, but its N-substituted derivatives can be studied in hexane by diluting the latter with a dioxan solution[7]. For the N-methyl, N-ethyl, and N-phenyl derivatives of acridone it has been possible to obtain a quasi-line structure for the $\pi-\pi^*$ phosphorescence band, in which the frequencies of the skeletal vibrations are active. Although the vibrational frequency of the C=O group appears in the spectrum, it is not the predominant frequency.

Phthalimides and naphthalimides. Although the absorption and phosphorescence spectra of phthalimide and its N-substituted derivatives in solid glasses at 77°K show a coarse vibrational structure[113-115], the first attempts to obtain the quasi-line structure of the absorption bands in n-hydrocarbons were unsuccessful[114,115]. This was due chiefly to the low solubility of the phthalimides in n-hydrocarbons. Phthalimide itself is almost insoluble, and its N-substituted derivatives readily precipitate from solution on cooling to 77°K, so that the concentration is insufficient for observation of the absorption spectrum of the solution, We were able[116] to obtain the quasi-line structure of the phosphorescence spectrum of N-methylphthalimide in hexane at 77°K; the spectrum consisted of a large number (more than 30) of closely situated quasi-lines. There are no predominant frequencies in the structure, and intervals close to the frequency of the stretching vibration of the C=O group do not appear distinctly. This characteristic feature of the structure is an important additional argument for assigning the phosphorescence of phthalimide to the $\pi-\pi^*$ transition.

The molecule of naphthalimide differs from that of phthalimide in its more extensive π system, and this leads to a different arrangement of the singlet and triplet $n-\pi^*$ and $\pi-\pi^*$ levels and the production of fluorescence in naphthalimide. In hexane at 77°K the fluorescence spectrum consists of a broad diffuse band, on which a number of narrow intense bands are superimposed. Better resolution of the structure could not be obtained in n-hydrocarbons, however.

Thioindigoids and indigoids. Nurmukhametov and coworkers[5,117,118] studied the vibronic spectra of thioindigoid and indigoid dyes, to investigate the nature of the electronic transition determining their colours. The fluorescence spectrum of thioindigo[118,119] is resolved in hexane and heptane into 12 narrow bands, which are less distinct in other n-hydrocarbons, beginning at octane. These bands were interpreted from the initial resonance O–O band at 18 308 cm^{-1} (in hexane) by means of the frequencies 220, 480, and 1540 cm^{-1}. The last frequency is the most characteristic in the spectrum, and it combines with the other frequencies, and this determines the two-fold repeated form of the structure of the emission band. The nature of the distribution of intensity in the spectrum indicates that the transition is allowed by symmetry and the Franck–Condon principle. The 1540 cm^{-1} frequency is assigned to the stretching vibration of the central ethylenic group. A similar structure is observed in absorption, interpreted by means of the frequencies 220, 480, and 1500 cm^{-1}. Although the molecule contains two carbonyl groups, their characteristic frequencies, which according to the infrared spectra of thioindigo should have the value 1650 cm^{-1}, do not appear in the structure. A possible explanation is that the long-wave transition of the thioindigo molecule is a $\pi-\pi^*$ transition, in which the excitation energy is concentrated to a large extent on the C=C group, and not on the C=O groups, as in an $n-\pi^*$ transition. This interpretation of the spectrum of thioindigo agrees with its ready cis-trans photoisomerisation, established by Rogers, Margerum, and Wyman. Photoisomerisation requires concentration of the excitation energy in the C=C bond.

The structure of the spectra of various derivatives of thioindigo and related molecules[13], whose formulae are given in Table 3, have also been studied. Their spectra preserve the general characteristic features of the thioindigoid spectrum.

Table 3. Vibronic spectra (at 77°K) of arytoxadiazoles, arylbenzoxazoles, thioindigoids, and indigoids (absorption and fluorescence).

Compound	References	Compound	References
2,5-Aryloxadiazoles		2-Phenylnaphth-[2,1d]-	97
Biphenyl-	92	2-Biphenylylnaphth-[2,1d]-	97
Bis(biphenylyl)-	92	1,4-Di-(2-benzoxazolyl)benzene	22, 96
Phenyl-β-naphthyl-	92	1,4-Di-(2-benzoxazolyl)ethylene	22, 96
Di-β-naphthyl-	92	Thioindigoids and indigoids	
Phenyl-α-naphthyl	92	Thioindigo	120, 121
Di-α-naphthyl-	92	5,5′-Dimethyl-	120, 121
α-Naphthyl-β-naphthyl-	92	6,6′-Dichloro-	120, 121
α-Naphthylstyryl-	92	6,6′-Diethoxy-	120, 121
Arylbenzoxazoles and arylnaphthoxazoles		5,5′-Dinitro-	120, 121
		6,6-Dinitroindigo	122
2-Phenylbenz-	22, 96	5,5′,7,7′-Tetrabromo-	122
2-Biphenylylbenz-	22, 96	5,5′,7,7′-Tetrachloro-	122
2-Styrylbenz-	22, 96	5,5′-Dichloro-	122
2-Phenylnaphth-[1,2d]-	97	NN′-Dimethyl-	122

Although the indigo molecule differs from that of thioindigo only in the replacement of S atoms by NH groups, the colours differ significantly: crystals of the former are deep blue, whereas those of the latter are red. For isolated indigo and thioindigo molecules, the differences in absorption are much smaller. Study of the structure of the vibronic spectra of these molecules has made possible

a more valid explanation of their common and individual properties. Indigo does not dissolve directly in n-hydrocarbons. The structure of the fluorescence and absorption spectra were obtained at 77 °K by diluting the dioxan solution with hexane in the ratio 1 : 15.[5,117] The form of the structure is similar to that for thioindigo, but the range of the spectrum is shorter, the number of bands is smaller (6), and the intensity of the O–O band with frequency 16 440 cm^{-1} relative to the other vibronic bands is much higher. The definite similarity in the quasi-line spectra of thioindigo and indigo indicates that their colours are determined by electronic transitions of the same character, and the main contribution to the excited state is made by the C=C group, whose vibrational frequency is most characteristic for the structure of the band due to this transition. The –NH– bridges in indigo are stronger auxochromes than the –S– bridges in thioindigo, leading to a more marked (by 1900 cm^{-1}) bathochromic shift in the band and a higher intensity for the O–O band.

Study of indigo derivatives (see Table 3)[5,117] showed that halogeno substituents have little influence on the structure and position of the fluorescence spectrum, showing their greatest influence on the relative intensity of the O–O band and leading in some instances to a more diffuse structure. Methylation of the NH group leads to a marked bathochromic shift and a decrease in the sharpness of the structure of the electronic bands. The low solubility of the indigoids is due to their marked association, and this is due chiefly to strong intermolecular hydrogen bonds, as shown by Shigorin and coworkers for the example of indigo molecules, which are associated by means of hydrogen bonds. This association is also responsible for the significant difference in the colours of indigo and thioindigo (the molecules of the latter cannot form hydrogen bonds with one another).

Porphyrins and phthalocyanines. Personov and Litvin[120,121] were the first to apply Shpol'skii's method successfully to compounds of these classes, which are of considerable biological importance. The three broad fluorescence bands observed under ordinary conditions for phthalocyanine without metal are resolved in octane at 77 °K into more than 30 bands, lying in the range 6840–7775 Å, with characteristic doublet splitting ($\Delta\nu$ between doublets 60 cm^{-1}). The 6939/6910 Å doublet has absorption bands which coincide by resonance. The spectrum of the long-wave absorption band is approximately the mirror image of the fluorescence spectrum and extends from 6939 Å to 6248 Å. Quasi-line long-wave absorption and fluorescence spectra have also been obtained for magnesium phthalocyanine; each is resolved into more than 30 bands, and there is a complex multiplet structure. The fluorescence spectrum of protoporphyrin in octane consists of a large number of doublets with $\Delta\nu = 20$ cm^{-1}, and can be interpreted satisfactorily by means of the vibrational frequencies 240, 740, 790, 985, 1135, 1225, 1345, 1550, and 1585 cm^{-1}.

Personov[121] made a detailed study of the quasi-line spectra of phthalocyanine in octane, nonane, and decane at 77 °K, and gave a detailed vibrational analysis. He pointed out the change in the distance between the doublets in different solvents, and on the basis of the fine details of the structure he concluded that in the range of the long-wave absorption, the fine structure of the overlapping bands of two electronic transitions with λ_{0-0} (I) = 6907/6917 Å (in decane) and λ_{0-0} (II) = 6506/6530 Å (in decane) is observed.

Shkirman and Solov'ev[122] obtained the quasi-line absorption and fluorescence spectra of tetrabenzoporphin and tetrazaporphin in octane at 77 °K. Because of their low solubilities, the former was dissolved first in chlorobenzene, and the latter in a pyridine–acetone mixture. The tetrazaporphin bands consist of complex multiplets, in which two components are the most intense. The intense doublet of the O–O band is observed at 6115/6134 Å with $\Delta\nu = 51$ cm^{-1}. The fluorescence and absorption spectra are almost mirror images and were interpreted by means of 17 vibrational frequencies. The quasi-line spectra of tetrabenzoporphin consist of characteristic doublets with intense resonance lines at 6580/6594 Å, with an interval $\Delta\nu = 32$ cm^{-1} between them. The fluorescence and absorption spectra are not mirror images. The quasi-line spectra of porphin and dihydroporphin (chlorin) in octane and decane at 77 °K have been described[123]. These compounds were dissolved in n-hydrocarbons through a buffer benzene solution. The fluorescence and absorption spectra of porphin consist of series of triplets with a resonance triplet of the O–O transition at 6127/6134/6149 Å (in octane). The structure of the fluorescence spectrum was interpreted by means of the frequencies 155, 310, 720, 786, 955, 974, 1014, 1057, 1176, 1222, 1263, 1319, 1361, 1389, 1409, 1456, 1497, 1539, 1605, and 1615 cm^{-1}. The spectrum of chlorin contains approximately the same frequencies, with the exception of the frequencies 786, 1176, 1319, 1456, and 1605 cm^{-1}. These frequencies of porphin are assigned to the symmetry species b_{1g}. Since in porphin the O–O transition is assumed to be forbidden by symmetry, these frequencies remove the forbidden character. The symmetry of the chlorin molecule is lower, and the transition is allowed by symmetry, so that only the completely symmetrical vibrations are active in its spectrum.

The absorption and luminescence spectra of azo-compounds and azomethine compounds have been studied in n-hydrocarbons and other solvents[124–127]. It was established that arylazo-compounds with general formula Ar-N=N-Ar′ become fluorescent only when an *o*-hydroxy substituent is introduced into the aryl ring; intramolecular hydrogen bonding then leads to the formation of a six-membered ring containing the –N=N– azo-group. The luminescence spectra of hydroxyazo-compounds are resolved only into a few broad bands. A similar picture is observed for the spectra of hydroxyazomethine compounds, in which the hydroxyl group is introduced into the aldehyde ring and forms a stable intramolecular hydrogen bond. Azomethines also become fluorescent when the $-N(CH_3)_2$ substituent is introduced into the *p*-position of the phenyl rings. From the example of α-hydroxyanthraquinones, hydroxyazo-compounds, and hydroxyazomethine compounds, it may be concluded that when an intramolecular hydrogen bond is formed, the electronic bands usually have a diffuse structure, but the increase in symmetry in the dihydroxy- and tetrahydroxyanthraquinones is accompanied by improved resolution of the structure. A less sharp structure compared with the spectra of benzophenones is also observed for *o*-hydroxybenzophenones.

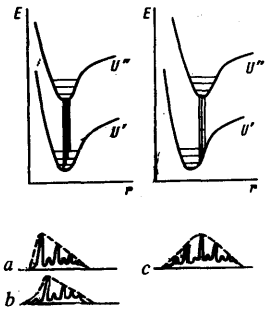
Shpol'skii's method has been used chiefly to resolve the structures of the electronic bands of luminescent molecules. In principle, however, it can also be used to obtain the quasi-line absorption spectra of non-fluorescent molecules. This can be illustrated by azobenzene, which does not exhibit luminescence. Dyck and McClure studied the absorption spectrum of an azobenzene–bibenzyl mixed crystal at 77 °K and 4 °K and found that whereas the long-wave $n-\pi^*$ absorption band does not show a resolved structure, the position and vibrational structure of the $\pi-\pi^*$ absorption band are similar to those of the absorption band of stilbene. Finally, triplet–triplet absorption bands have been observed under the conditions of Shpol'skii's method[128,129].

3. THE VIBRONIC SPECTRUM AND THE STRUCTURE OF MOLECULES

Electronic transitions in molecules differ in the type of excited state ($n-\pi^*$ or $\pi-\pi^*$) realised in the transition; in whether the transition is allowed or forbidden by symmetry or the Franck–Condon principle; and in whether the transition can take place between states with the same multiplicity—singlet–singlet or triplet–triplet—or different multiplicities—singlet–triplet. All these features determine the nature of the electronic transition, which has a significant influence on the form of the vibrational structure.

When the transition is allowed by symmetry, the band due to the purely electronic transition in the system of vibronic bands is clearly distinguished in the spectrum and has a comparatively high intensity (if it is forbidden by other reasons, for example by the Franck–Condon principle). The frequencies of the completely symmetrical vibrations, chiefly those of the framework containing the electronic system excited in the transition, predominate in the structure of the band. In the case of hydrocarbons these are the vibrational frequencies of the carbon framework of the π system. The values of the frequencies in the fluorescence and phosphorescence spectra (in which the vibrations of the ground electronic state appear) coincide with or are very close to the values of the frequencies found in the Raman spectrum of the same compound. In the absorption spectra, however, the same vibrations may have slightly altered frequency values, and this makes the identification of the type of the vibrations difficult. Thanks to the mirror symmetry rule, however, identification is often possible, so that the change in the vibrational frequencies in different electronic states can be estimated. The structure may reveal not only the completely symmetrical vibrations, but also a certain type of incompletely symmetrical vibration, namely those in which the transition is still allowed by symmetry but in which the direction of its polarisation changes. This was shown in a series of papers by Zimmerman and Yoop[130-135] on the study of the polarisation absorption and fluorescence spectra at −180°C for alcoholic solutions of naphthalene, phenanthrene, anthracene, tetracene, tetraphene, chrysene, pyrene, perylene, and azulene. Dörr and coworkers[136-138] showed that the incompletely symmetrical vibrations which rotate the plane of polarisation of the vibronic oscillator through 90° appear in the phosphorescence spectra of a number of aromatic hydrocarbons. Shpak and Malykhina established that the fluorescence spectrum of stilbene contains two mutually perpendicular polarised band series. Naphthalene, phenanthrene, and pyrene provide examples of molecules in whose quasi-line spectra it has been possible to observe incompletely symmetrical vibrations. Bolotnikova found that the fluorescence spectrum of naphthalene in pentane at 77°K shows the 495 cm^{-1} frequency of the vibration with symmetry b_{1g}; the frequencies of the completely symmetrical vibrations combine with it to form a second series of bands which are polarised, in agreement with McClure's studies, in a direction perpendicular to that for the first series of bands, beginning from the initial purely electronic O–O band. Analysis of the quasi-line fluorescence and phosphorescence spectra of phenanthrene enabled Pesteil and Rabaud[40] to distinguish in the spectrum the frequencies of the normal vibrations, the number of which is greater than the total number of completely symmetrical vibrations. On this basis, using data from the vibrational spectra, these authors assigned some of the frequencies to definite incompletely symmetrical vibrations. Klimova[43] established that the spectra of pyrene show the frequencies of incompletely symmetrical vibrations.

When the transition is forbidden by symmetry, the purely electronic band either is not observed or has a low intensity. The forbidden character resulting from symmetry is removed in this instance by the superposition of a definite type of incompletely symmetrical vibration on the electronic transition. The corresponding vibronic band is more intense than the purely electronic band and serves as the origin for progressions of the frequencies of the completely symmetrical vibrations. These electronic bands are characterised by example *b* (see Figure) of the distribution of band intensity along the spectrum, if in the excited state the equilibrium interatomic distances are close to the distances in the ground state. This type of vibrational structure (low intensity of the purely electronic band, removal of the forbidden character by a quantum of the incompletely symmetrical vibration, and distribution of the band intensity along the spectrum according to example *b*) is observed in the spectra of the molecules of benzene, coronene, and triphenylene, which have an O,O transition forbidden by symmetry. A similar picture is observed in the spectra of biphenyl and naphthalene, where the purely electronic transition is partly forbidden.



Different examples of the distribution of intensity in the vibronic bands: *a*) for an electronic transition allowed by symmetry and $r_0' = r_0''$; *b*) for a transition forbidden by symmetry and $r_0' = r_0''$; *c*) for a transition between states with $r_0'' > r_0'$; u' and u'' are the potential curves of the ground and excited states, and r_0' and r_0'' the equilibrium distances in these states.

If however the electronic transition takes place into a state with significantly altered equilibrium distances, the purely electronic transition is forbidden or greatly weakened as a consequence of the Franck–Condon principle, and the system of bands for this transition is characterised by example *c* of the distribution of intensity within this system (see Figure). This is observed for the $n-\pi^*$ transitions of carbonyl-containing molecules, as shown for a number of aromatic aldehydes and ketones, anthraquinone, etc.

Thus from the relative intensity of the purely electronic band it is possible to obtain information on the degree of allowed character (or forbidden character) of the electronic transition, and from the form of the intensity distribution it is possible to obtain information on the forbidden character of the transition.

The form and degree of resolution of the structure are closely related to the nature (type) of the electronic transition, and this is reflected in one of the distinguishing criteria for $n-\pi^*$ and $\pi-\pi^*$ bands. Kasha [73] pointed out that the structure of $n-\pi^*$ bands is usually exceptionally sharp for vapours, but is much less sharp in the condensed phase (liquid and solid solutions), whereas the structure of the $\pi-\pi^*$ bands is more diffuse in vapours, and improvement in the resolution of the structure is observed in solutions, particularly at low temperatures. It should be noted that these differences do not always emerge clearly. For example, for molecules with a non-rigid and non-planar structure, both the $n-\pi^*$ and $\pi-\pi^*$ bands are often structureless (the influence of spatial configuration on structure will be examined below). In those instances, however, where structural factors do not lead to a decrease in the sharpness of the bands, the formulated criterion for bands due to $n-\pi^*$ transitions is applicable only for singlet–singlet transitions, that is for the $n-\pi^*$ absorption bands and for $n-\pi^*$ fluorescence, when this takes place.

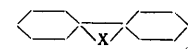
Resolution of the quasi-line structure is possible for the $n-\pi^*$ fluorescence bands, as demonstrated for the molecules of anthraquinone, anthrone, xanthone, etc. Under those conditions favouring the resolution of the vibrational structure, the $n-\pi^*$ absorption band remains structureless or shows little structure, whereas resolution of the structure is observed for the absorption bands of the higher $\pi-\pi^*$ transitions. If in a molecule the $n-\pi^*$ levels lie above the $\pi-\pi^*$ levels for a definite change in the structure of the molecule, the $\pi-\pi^*$ absorption, fluorescence, and phosphorescence bands may show a quasi-line vibrational structure (α- and β-naphthaldehydes, N-methylphthalimide, and N-substituted derivatives of acridone provide examples of molecules with $\pi-\pi^*$ phosphorescence and a resolved structure). The close relationship between the form of the vibrational structure and the nature of the electronic transition provides new possibilities for obtaining information on this transition from the characteristic features of the structure of the band.

Dependence of the vibrational structure of the electronic bands on the three-dimensional structure. For molecules of aromatic hydrocarbons (with the same type of $\pi-\pi^*$ transitions) with a rigid structure it is possible in most instances to select conditions for distinct resolution of the structure. The introduction into these molecules of alkyl and halogeno substituents, which have little influence on the energy and nature of the $\pi-\pi^*$ transitions, may influence the form of the structure and its degree of resolution in different ways. Various examples of the spectra of halogeno-derivatives (halogenonaphthalenes, halogenoanthracenes, and halogenopyrenes) show that despite the strongly polar character of the C–halogen bond, which should lead to intensification of the interaction between the dissolved molecule and the solvent, the introduction of halogen usually is not accompanied by a marked decrease in the sharpness of the structure. Moreover, the change from pyrene to halogenopyrenes is accompanied by the same decrease in the width of the quasi-lines at 77°K as is observed for the spectra of pyrene on going from 77°K to 4°K.

The spectra of aromatic hydrocarbons (polyphenyls, diphenylpolyenes, and arylethylenes) usually consist of more diffuse bands, particularly for molecules with sterically hindered groups. For example, the electronic bands of biphenyl show a clearly defined structure, which becomes less distinct when α-alkyl substituents are introduced. The absorption and fluorescence bands of trans-stilbene have a clearly defined structure, whereas the absorption bands of cis-stilbene are structureless, and fluorescence is not observed.

Although a non-planar structure leads to significant weakening of the π-conjugation, so that the aryl fragments of the molecule are chiefly responsible for the electronic bands, these bands nevertheless show a clearly defined structure, which is similar to that of the bands for the hydrocarbons corresponding to this fragment. A bridge with extensively weakened conjugation begins to play the part of a substituent. This picture was observed for β-binaphthyl and the cis-isomer of di-(9-anthryl)ethylene.

The introduction of bridges which fix the planar structure but do not alter the π system leads to more distinct resolution of the structure.

In substituted aromatic compounds with an electron-donating group $-NR_2$, $-NR-$, $-OR$, $-O-$, $-SR$, or $-S-$, the unshared pair of electrons of the heteroatoms X = N, O, or S is conjugated with the π electrons, and their electronic bands are determined by the excitation of the complete π ($2p_z$) system of electrons. These π,π^* ($2p_z$) bands have certain characteristic features, some of which are due to the incomplete conjugation of the $2p_z$ electrons of the heteroatom with the π electrons. Kasha [139] pointed out that because of the nature of the hybridisation, the orbitals of the unshared pairs of these heteroatoms are not strictly parallel to the p orbitals of the π electrons, but may lie at an angle to them, leading to incomplete π conjugation. To this he attributed the slightly lower values of the absorptivities ϵ of the absorption bands due to the $\pi-\pi^*$ ($2p_z$) transitions compared with those for the bands of the resolved $\pi-\pi^*$ transitions, and also the decrease in the lifetime of the phosphorescence (that is the increase in the probability of triplet–singlet conversion resulting from the fact that the $2p_z$ orbital of the heteroatom, lying at an angle to the p orbitals of the π system, as it were occupies an intermediate position between the p orbitals and the n orbitals which are perpendicular to the p orbitals). Since these electron-donating groups can rotate relative to the C–X bond, the angle of slope of this orbital will generally be different in different electronic states. This is apparently one of the chief reasons for the lack of sharpness of the structure in the spectra of aromatic amines, alcohols, ethers, and thioethers to the extent that their bands show only a coarse structure, and not a quasi-line structure. Convincing evidence in support of this is provided by the fact that the electronic bands show a quasi-line structure when the $-NR-$, $-O-$, or $-S-$ bridges are included in a rigid ring. Nurmukhametov and Gobov [98] demonstrated this for molecules with general formula  where X = NH (carbazole), O (diphenylene oxide or dibenzofuran), or S (diphenylene sulphide). Nurmukhametov and coworkers [7] obtained the same result for the molecules of acridan (9,10-dihydroacridine), xanthone, and N-substituted derivatives of acridone.

Another factor leading to a decrease in the sharpness of the spectra of compounds of this type is the high sensitivity of their electronic bands to the nature of the solvent. A marked displacement of the bands is usually observed for these compounds on going from a non-polar solvent to a polar solvent. The presence of small quantities of polar impurities in n-hydrocarbon solvents is therefore sufficient for the formation, in the solution, of molecular centres with appreciable dispersion of the frequencies of the electronic transitions. A unique example of the departure from a planar structure as a result of interaction of the electrons of an unshared pair with π electrons is provided

by benzylideneaniline, in which the N-phenyl ring is turned out of the plane by 60°, so that the molecule acquires the energetically most favourable spatial configuration. The introduction of an –O– bridge (the phenylbenzoxazole molecule) leads to a planar structure for the molecule, in which the n electrons are now not conjugated with the π electrons of the N-phenyl ring. Benzylideneaniline shows broad absorption bands and no fluorescence, whereas the absorption and fluorescence bands of 2-phenylbenzoxazole show a clearly defined quasi-line structure.

4. SPECTROSCOPIC-ANALYTICAL APPLICATIONS

The highly characteristic nature of quasi-line electronic spectra has found extensive application as a basis for the development of spectroscopic-analytical methods for the detection and quantitative determination of small quantities of organic substances. On the basis of the quasi-line luminescence spectra it has been possible to achieve the high sensitivity in the determination of traces of organic compounds (down to 10^{-12} M) which was previously attained only for inorganic compounds. The fact that the luminescence light in these spectra is collected into narrow quasi-line bands makes it possible to carry out an analysis at "noise level", that is when the luminescence of other trace materials in the same range has an intensity comparable with that of the compound being determined. The high sensitivity, the speed of the analysis, the unlimited reproducibility in a given specimen, and the fact that the specimens to be analysed do not have to satisfy special requirements make analytical methods based on Shpol'skii's spectra very effective and promising. The analytical applications have been developed chiefly for substances which exhibit fluorescence in the visible range. Shpol'skii's spectra have proved very effective for the detection and determination of carcinogenic aromatic compounds. Carcinogenic substances have been detected and their concentrations determined in atmospheric air [140,141], tobacco smoke [142], industrial products [143], and in various smoked products [144]. Work on the detection and identification of individual aromatic compounds in bitumens and petroleums has been carried out by Il'ina and coworkers [145-147], who unambiguously identified perylene, 1,12-benzperylene, coronene, and pyrene in the naphthenic–aromatic fractions of bituminous substances. Utkina [148], without preliminary chromatography, determined a number of aromatic hydrocarbons of the anthracene–phenanthrene fraction of coal tar.

A series of papers by Teplitskaya and coworkers [149-154] described the use of Shpol'skii's spectra in the analytical determination of organic substances in rocks of different origin, meteorites, and minerals. The organic substances are present in rocks in small quantities (10^{-4}–10^{-1}% [154]) and the concentration of aromatic hydrocarbons to be determined often amounts to only 10^{-7}%. The authors cited [149-154] were able to determine organic substances in rocks even when this was impossible by other analytical methods. Teplitskaya [149] was the first to detect a number of polycyclic aromatic hydrocarbons in igneous rocks, using Shpol'skii spectra. The individual composition of the carbonaceous material in igneous rocks has been studied [151] and it has been established that calcite from the Darasun deposit contains 1,12-benzperylene, 3,4-benzpyrene, and various other unidentified aromatic compounds.

By means of Shpol'skii's spectra, it has been possible for the first time to identify the individual organic substances present in meteorites; before this, it was considered an achievement to determine even the group composition of the organic material in meteorites. Teplitskaya and coworkers [152] identified a number of individual compounds—anthracene, 3,4-benzpyrene, 1,12-benzperylene, and coronene—in extracts obtained from meteorites—carbonaceous chondrites. The authors cited [152] also observed a similarity in the compositions of the polycyclic aromatic hydrocarbons in the organic material from carbonaceous chondrites, rocks, and minerals of endogenic origin.

Interesting results were obtained by Teplitskaya and coworkers [153] in a study of the spectra of the mineral hackmanite, which exhibits phototropic properties. Some specimens of hackmanite show a pink-red colour, which becomes paler under the influence of daylight. This colour is restored in the dark or under the influence of ultraviolet light. The luminescence spectrum associated with the red colour centres of hackmanite shows a structure at 77°K similar to the structure of the spectra of thioindigoids. On this basis, these authors [153] put forward the new suggestion that the colour centres in this instance are organic sulphur-containing compounds. The presence of aromatic compounds was established from the quasi-line spectra in extracts of organic substances from hackmanite.

Shpol'skii's method has also been used as a basis for the development of quantitative methods of spectrochemical analysis. Personov and Teplitskaya [155] developed a method for the quantitative determination of small quantities of perylene and 1,12-benzperylene from their quasi-line fluorescence spectra, and achieved a high sensitivity (down to 10^{-11} g ml^{-1}) with an accuracy of 10–20%. Quantitative methods for the determination of the strongly carcinogenic 3,4-benzpyrene from the quasi-line spectra were described by Muel and Lacroix [156], Dikun [157], Personov [158], and Khesina [159]. Photoelectric recording [156,158,159] or photographic recording [157] were used. Muel and Lacroix determined the concentration by the method of additions, and Personov used the method of internal standards; the latter achieved a sensitivity of 10^{-9} M with an accuracy of 7–15%.

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Extensive possibilities are provided by Shpol'skii's spectra in photochemical studies. Personov [52] observed the photochemical transformation of perylene in chloroform under the influence of daylight. The product of the photoreaction, tentatively regarded as a chloro-substituted perylene, gave a quasi-line fluorescence spectrum in hexane solution at 77°K, displaced towards lower frequencies by ~ 400 cm^{-1}.

Gobov and coworkers [89] showed that ultraviolet irradiation of a solution of di-α-naphthylethylene produces a photoproduct for which the quasi-line structure of the fluorescence and phosphorescence spectra indicated the presence of naphthyl nuclei in the molecular structure. Later, Nurmukhametov and Grishina [160] proved unambiguously that these spectra are due to the hydrocarbon picene, produced by the photocyclohydrogenation of di-α-naphthylethylene.

Intensive studies are now being made of the widely encountered reaction of photochemical cyclisation (photocyclodehydrogenation), by means of which polycyclic condensed hydrocarbons are formed from arylethylenes (for example phenanthrene from stilbene), the corresponding substituted polycyclic hydrocarbons are obtained from substituted arylethylenes, N-heteroaromatic polycyclic compounds are obtained from the N-heteroanalogues of arylethylenes, etc. The photocyclisation products are characterised by a more rigid molecular structure, and

hence by electronic bands with a clearly defined vibrational structure. The use of Shpol'skii's spectra to study these reactions opens up the possibility of ready, rapid, and unambiguous identification of the photocyclisation products and the possibility of studying the kinetics of the reaction by spectroscopic methods. Nurmukhametov and Grishina[161] unambiguously established from the quasi-line spectra the formation of chrysene from α-naphthylphenylethylene, 3,4-benzphenanthrene from β-naphthylphenylethylene, and 1,12-benzperylene from di-β-naphthylethylene.

The application of Shpol'skii's method to the detection and identification of aromatic radicals appears attractive. Grajcar and Leach[63] used the characteristic structure of the fluorescence spectrum in the region of 4600 Å to establish the formation of the benzyl radical when a solution of toluene in methylcyclohexane + 3-methylbutane (2 : 3), frozen at 77°K, was irradiated by light with wavelength 2537 Å (λ_{Hg}). Mileshina and coworkers[65] observed the production of green luminescence during the photolysis of diphenylketen in hexane at 77°K. On the basis of an analysis of the quasi-line spectrum of this luminescence, together with electron paramagnetic resonance data, it was shown that the biradical of diphenylmethylene is formed from diphenylketen.

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Karpov Physicochemical
Institute, Moscow

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The Development of Russian Chemistry and the Mendeleev Society† (The Centenary of the All-Union D.I.Mendeleev Chemical Society)

S.I.Vol'fkovich

A hundred years ago chemistry in Russia was represented by several score scientists, chiefly teachers, whose research interests were mostly concerned with the analysis of naturally occurring substances and their technological application. Only a few Russian scientists were engaged in theoretical studies on the borderlines between chemistry and physics, and investigations of organic syntheses only began in the middle of the last century.

M. V. Lomonosov's genius introduced fundamental concepts into many aspects of theoretical and practical chemistry, and foresaw the lines of development of chemistry for centuries to come; Lomonosov left a scientific legacy which exercised an immense influence over the subsequent advances of Russian chemistry.

Two scientists are regarded by science historians as the founders of the first large schools of chemistry in Russia: firstly, A. A. Voskresenskii, Professor at the Chief Pedagogical Institute, St. Petersburg, and at the University of St. Petersburg, who trained a number of generations of chemists including D. I. Mendeleev, N. A. Menshutkin, P. A. Il'enkov and others, justifying his reputation as the "grandfather of Russian chemists"; and secondly, N. N. Zinin, Professor at Kazan University and later at the Medical and Surgical Academy at St. Petersburg, whose students included, among others, A. M. Butlerov and A. N. Engelgardt.

Voskresenskii's and Zinin's outstanding activities reached their peak during the Forties and Fifties of the last century.

In 1854–1857, in St. Petersburg, P.A.Il'enkov, N.N.Sokolov, A. N. Engelgardt and several other chemists organised two small groups who used to meet at their houses to exchange the results of their work, help one another and engage in lively discussions of the ways to advance chemical industry and chemical education. Sokolov and Engelgardt equipped a private laboratory at home for the members of their group, offering facilities for those who wanted to experiment or to try out experimental techniques. The laboratory proved to be a great success. However, after only 3 years it had to be abandoned because of a lack of funds, and all the equipment was donated to St. Petersburg University, where Sokolov went in 1860 to deputise for D. I. Mendeleev, who was abroad. At that time, the chemical laboratory for the University students consisted of a single room, and the chemical laboratories of the Academy of Sciences numbered 4 rooms. This brief reference shows that the organisers of the abovementioned groups were active, forward-looking and public spirited men. Their biographical backgrounds are also interesting. Sokolov was a Law graduate of St. Petersburg University, who then joined the Natural Philosophy Faculty, graduating as Candidate of Philosophy. He worked for several years in various chemical and physical laboratories in Germany and France; then he studied the natural deposits of the Urals; eventually he became interested in organic chemistry, obtained his Doctorate, and embarked on courses of lectures in general and organic chemistry, which were brilliantly presented and greatly appreciated by students. Engelgardt graduated from the Artillery Academy, became interested in chemistry, retired, and began teaching chemistry at the Institute of Forestry. He was awarded a doctorate by St. Petersburg University, without defending a thesis, for his work on the

† An augmented paper given on 24th October 1968, at the Palace of Congresses in Moscow, at the plenary meeting to celebrate the Centenary of the All-Union D. I. Mendeleev Chemical Society, by the Society's President, S. I. Vol'fkovich.

Kursk phosphorites and on the development of the methods of alkali treatment of bones, among other topics. In 1870 he was arrested for being a member of the "Land and Liberty" party, and after serving a term of imprisonment at the Petropavlovsk fortress he was exiled from St. Petersburg and deprived of the right to live in University towns. He settled at the Batishchevo estate in the Smolensk region, where he lived for many years, working on agricultural problems, especially experiments on the use of phosphorites and the development of agricultural technology. It was not until 1880 that Engelgardt regained his right to free movement, through the good offices of the Russian Chemical Society. Lenin is known to have read Engelgardt's articles "Letters from the Country" with interest, noting their educational and populist bias.

Mendeleev took an active part in these groups, showing from the very start of his scientific and teaching career great social initiative, putting forward bold and original ideas. He never undertook any work or proposed any hypotheses without public discussion, at the same time taking an interest in the work of others and assessing it critically; also he always maintained close contact with Russian industry and with foreign scientists. Other members of these groups were also socially aware and progressive men.

They soon came to feel the need for attracting wider circles of chemists in order to enhance the scope of the work in various areas of chemistry. A proposal was made to organise an officially functioning Society.

Until 1868 a number of chemists were members of the oldest Russian scientific Society, whose membership was made up of widely varying specialists—the Free Economic Society (founded in 1765) and of the Russian Technical Society (founded in 1866), whose members were mostly connected with industry. Advances in chemistry and increasing specialisation created a need for more profound and many-sided contact between people working in chemistry, at that time still not a very popular science, and largely unfamiliar to many engineers, technologists, biologists, economists and other specialists.

THE FIRST FIFTY YEARS

The Eighteen-Sixties in Russia were a period of important social developments. The abolition of serfdom, the beginnings of capitalism and the first steps towards the exploitation of native natural resources had a great influence on the Russian intelligentsia.

The first congress of Russian natural scientists, called together on the initiative of the Chemical section, took place in St. Petersburg from 28th December 1867 to 4th January 1868 and adopted a resolution stating that it was desirable to organise a Chemical Society which would "have members in all Russian cities" and whose publications would include "the work of all Russian chemists". A special commission worked out the constitution of the Russian Chemical Society, and on 1st October 1868 the first organisational meeting of the Society took place under the chairmanship of G. G. Gustavson, at which Mendeleev reported on the views of the Scientific Committee of the Ministry of Public Education concerning the projected constitution of the Society. The constitution was approved by the Ministry on 6th November. At the first meeting of the Russian Chemical Society, with a membership of 35, on 18th November 1868 N. N. Zinin was elected President and N. A. Menshutkin—Secretary. The latter was Editor of the Society's Journal, which first appeared in 1869, for thirty years.

The Physical Society, which was organised in 1872 at St. Petersburg University, amalgamated with the Chemical Society in 1878 to form the Russian Physico-Chemical Society which soon acquired great authority and international popularity. This was especially due to the fact that the Society's Journal and the Society's members' meetings became a focal point and forum for many outstanding communications, investigations and discoveries.

In 1878 A. M. Butlerov was unanimously elected President of the Society.

It is possible to state, without "jubilee exaggerations", that no serious chemical investigation went without a report to the Society or publication in Zhurnal Russkogo Fiziko-Khimicheskogo Obshchestva, which over a period of 62 years (1869–1931) published about six thousand papers; the Journal was taken by all chemical libraries and laboratories abroad. Mendeleev presented his work to the Society and published 135 of his papers in its Journal, where A. M. Butlerov published 58.

Russian chemists considered it an honour to give a paper at the Society's meetings or have a paper published by the Journal. In fact, the epoch-making report of Mendeleev's discovery of the Periodic Law of the chemical elements was made at the Society's meeting by N. A. Menshutkin, on the author's behalf since Mendeleev himself was ill, on 18th March 1869; the paper was entitled "The Relation of Properties to the Atomic Weight of the Elements".

A. M. Butlerov first presented his theory of the chemical structure of organic compounds to the Society.

The first report on the invention of radio was made by A. S. Popov in 1895 at a meeting of the Russian Physico-Chemical Society. D. N. Chernov, who created the science of metallography, also presented a paper at the Society.

From the first days of its inception the Society was interested in science and industry, and tried to promote the development of productive potential and the creation of a Russian chemical industry.

To encourage original work and to attract younger scientists to research, the Society established a series of commemorative prizes for the best research projects.

Apart from the discoveries by Mendeleev and Butlerov mentioned above, a number of other outstanding investigations were carried out by Russian chemists in the last century.

In 1842 N. N. Zinin discovered the reaction for the preparation of aniline which formed the basis of the aniline dyestuffs industry all over the world. His work on primary aromatic amines initiated the synthesis of a number of intermediate products, pharmaceutical preparations, nitroglycerine, etc. The important dye, fuchsine, was discovered by Ya. Natanson in 1855.

In 1840 Hess discovered one of the basic laws of thermochemistry—the law stating that the sum of the heats is constant‡. His text-book "The Fundamentals of Pure Chemistry" saw seven editions during the author's lifetime.

In 1838–1841 A. A. Voskresenskii obtained a new alkaloid —theobromine, which found extensive application in medicine—and quinone, whose derivatives became intermediates in dyestuffs synthesis.

Professor K. K. Klaus of Kazan University discovered a new element—ruthenium, in 1844 and studied a number of other platinum metals.

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‡ Hess formulated his law 2 years before the appearance of Meyer's publication and 7 years before Helmholtz indicated the general significance of the principle of the conservation of energy.

During the Eighteen-Forties B.S. Yakobi invented galvanoplasty, without applying for a patent so as to make the method available for universal use.

In 1868 A.N. Engelgardt first established the effectiveness of using phosphorites as fertilisers in acid soils; I.A. Il'enkov proposed in 1865 an alkali method for making bone fertilisers.

N.N. Beketov first isolated metals from their solutions by means of hydrogen under pressure (1862–1865) and developed the alumothermal method of obtaining pure metals by reducing their oxides with aluminium.

In September 1883 K.E. Tsiolkovskii sent a number of papers, among them "The Work of Gravity" and "The Mechanics of a Congruently Changing Organism" to the Journal, whose editors, P.I. Borgman and I.M. Sechenov, noted the author's ability. In 1897 Tsiolkovskii asked for his projected experiments on the dirigible to be considered, and, should they be found to be promising, for a grant of 200 roubles to be made from the Society's funds. The Society found the proposed experiments to be most important and much larger scale investigations to be essential. In 1900 on the recommendation of the Society, Tsiolkovskii was given a grant by the Academy of Sciences, for experiments with large models.

A series of original papers on periodic systems, on the "Evolution of the Worlds from a Modern Astrophysical and Geophysical Point of View", and others, was presented to the Society by the former inmate of the Schliesselburg Fortress, the Populist N.A. Morozov. It is remarkable that Morozov, despite 29 years of solitary confinement in Tsarist prisons, must have been the first to postulate a hypothesis of a radioactive origin of the planets and stars.

At the First Mendeleev Congress, D.N. Pryanishnikov reported the results of his investigations of root secretions and his original work on the nitrogen feeding of plants.

In the Seventies and Eighties V.V. Markovnikov studied in depth the composition of Caucasian oil and discovered a new type of hydrocarbon compounds—the polymethylenes.

In our time it is superfluous to talk of the world-wide importance of Mendeleev's Periodic Law, discovered in 1869 and of Butlerov's theory of the chemical structure of organic compounds; these are now familiar not only to chemists but also to all educated people. It is fitting, however, to mention here that Mendeleev and Butlerov made great contributions to other areas of chemical science, industry and agriculture, as well as to public life.

Mendeleev, Butlerov, Zinin, Menshutkin, Beketov and their colleagues can, like their contemporaries in music, be justly called the "mighty bunch" in chemistry. They were indeed giants in chemical science. Engels wrote in his "The Dialectics of Nature": "Mendeleev made an immensely important scientific achievement in unconsciously applying the Hegelian law of the transformation of quantity into quality..."

Several other chemists who carried out outstanding investigations at the end of the last century should be mentioned.

A.P. Borodin, Professor of Organic Chemistry, physician and composer, reported in 1869 to the Society his studies of the products of acetaldehyde condensation and the discovery of a new aldol compound.

I.G. Kucherov discovered and elaborated (1881) a method for preparing acetaldehyde by catalytic hydration of acetylene, which became widely used for the production of acetic acid.

In the Eighties, N.A. Menshutkin became one of the pioneers in the study of the kinetics of a number of important reactions and the relation between the reactivity and the composition and structure of organic compounds.

A.E. Favorskii discovered and studied the interconversions of acetylene hydrocarbons, thus laying the foundations of an extensive range of industrial processes.

In the Eighties and Nineties D.P. Konovalov discovered the laws determining the evaporation and boiling of binary liquid systems.

I.A. Kablukov first discovered in 1889–1891 anomalous electrical conductivity in solutions of electrolytes in non-aqueous organic solvents.

In the Nineties, A.N. Bakh formulated the peroxide theory of slow oxidation, which explained the action of oxidising enzymes, the mechanism of respiration and a number of other fundamental questions.

N.A. Shilov, in 1904, studied the nature of conjugated reactions and developed the methodological basis for anti-gas protection.

In 1905 L.A. Chugaev discovered the rule of cycles in the chemistry of complex compounds, prepared for the first time a series of organic platinum compounds, and pioneered the use of organic reagents in analytical chemistry.

A.E. Arbuzov published in 1905 the first paper in an extensive and important cycle of investigations of the structure, synthesis and properties of organo-phosphorus compounds.

At the beginning of the twentieth century A.V. Kistyakovskii developed a detailed oxide theory of the appearance of reticulate films which passivate metals, this was of practical importance in connection with anti-corrosion measures.

N.S. Kurnakov undertook, in the Nineties, a systematic study in depth of the relationship between the composition and the properties of metal alloys, salts and other systems, developing his studies over half a century and founding a large school of physico-chemical analysis.

V.N. Ipat'ev published in 1901 his catalytic methods of preparation of a series of organic compounds, at high pressures and temperatures (hydrogenation, decomposition and other reactions), which found application in the petroleum industry and the technology of other hydrocarbons.

In 1897 L.V. Pisarzhevskii and P.E. Melikashvili (Malikov) published in the Society's Journal their work on the structure and properties of the peroxide compounds of a number of metals and peracids.

At the beginning of this century M.S. Tsvet created a new adsorption method of analysis—chromatography, which now enjoys the widest application and further development not only in analysis but also in technology, for the separation of complex mixtures of substances.

V.I. Vernadskii deserves special mention for creating the new branches of science which combined chemistry with geology and biology—geochemistry and biogeochemistry—and for laying the foundations of extensive radiochemical investigations and a systematic study of Russia's productive potential.

N.D. Zelinskii is gratefully remembered for developing in 1915 a carbon gas-mask which saved the lives of many thousands of soldiers during the First World War; he also pioneered much work on catalytic transformations of hydrocarbons, petrochemistry, and the chemistry of proteins and other substances.

The list of outstanding research of the last century and the beginning of the present one could, naturally, be very much extended, but even the above selection suffices to illustrate the high level of originality and the fundamental significance of the investigations undertaken in the unfav-

ourable climate of pre-revolutionary Russia. All the research work mentioned above was either reported to the Society or published in its Journal.

In his speech at the annual meeting in 1924 the President of the Chemical Society in England, Wynne, stressed the great importance of the work of Russian chemists and advised young English chemists to study the Russian language in order to be able to read Russian publications in Zhurnal Russkogo Fiziko-Khimicheskogo Obshchestva in the original. Similar views were expressed by scientists in other countries.

It is worth mentioning that strong materialistic, progressive and democratic tendencies were characteristic of the Russian Chemical, and subsequently the Russian Physico-Chemical, Society. Many of its leading members repeatedly attacked the reactionary Tsarist regime and social oppression.

N. N. Zinin, N. N. Sokolov and others often spoke against idealistic philosophy, pointing out that it ignored the achievements of materialistic natural science.

Leading Russian chemists were sharply critical of Wilhelm Ostwald from the time of the appearance of his energetic teachings; in 1895 he read a paper entitled "The Untenable Nature of Scientific Materialism", rejecting atomic and molecular concepts. Mendeleev, Beketov, Vernadskii, Kablukov, Kurnakov, Kurbatov and many others were among the many chemists and physicists who defended materialistic concepts and the atomic-molecular theory. These discussions often appeared in the pages of the Journal. Mendeleev had this to say about Ostwald's views: "There are scientists who deny matter, since, they say, we know only energy .... matter is only energy .... such concepts ... cannot be entertained in any sane mind"[1]. Lenin is known to have considered Ostwald's views critically and in detail in his work "Materialism and Empiric Criticism", in which he called Ostwald "a very great chemist and a very confused philosopher"[2]. As the result of discussions and a series of experimental verifications, Ostwald was forced to admit, in 1908, that he had been mistaken.

In another guise, the pre-eminence of energy, and in particular, of electricity and electrification in relation to chemistry and its application formed the subject of numerous discussions[3-8]. G. M. Krzhizhanovskii wrote: "Chemistry is becoming a section of the general subject of electricity". The resolution of the Plenary Session of the Central Committee of the Communist Party of the Soviet Union dated 13th December 1963 states: "We can now say, with full justification, that Communism is Soviet power plus electrification of the whole country plus the application of chemistry to the national economy".

The Society has often discussed the economic problems of the chemical industry, including metallurgy, the production of building materials, the food, textile and other industries, as well as the production and use of mineral and organic fertilisers.

The Society's members have often expressed anti-Malthusian views. Mendeleev called the "theory" and proposals put forward by Malthus—"ravings", and D. N. Pryanishnikov, who gave a lecture on "Malthus and Russia"[9], said that "... for another 150 years Russia need not worry about the supplies of food, even if it doubled its population every 50 years".

Despite his dualism in some of his social and political views, Mendeleev was a true revolutionary not only in science and technology, but also in many state and public undertakings. He not only urged the industrialisation of the country and help for agriculture by industry, but also actively assisted this by his fundamental economic studies, his frequent visits to mines, industries, factories, agricultural and forestry concerns. He did much to promote higher education for women, encouraged cooperation, and despite the approaches of capitalist oil-producers and others, refused on principle any participation as a member or shareholder of their concerns.

Both Mendeleev himself and his closest friends were both great patriots and convinced internationalists who maintained friendly scientific contacts with chemists abroad.

In 1870, when the German chemists Kolbe and Volhard put forward nationalistic views, chauvinistically designed to debase the importance of French chemical research and elevate German work, Zinin, Butlerov, Mendeleev and Engelgardt published a protest against nationalism and chauvinism in science.

An excerpt from the telegram sent by the Russian Physico-Chemical Society in April 1906 to the French Physical Society on the death of Pierre Curie is interesting for ideological insight. It said: "Curie should be dear to all nationalities. He belonged to that part of the French people who work for the benefit of all humanity and do not serve the base interests of finance or reactionary governments".

Mendeleev was not only a man of the highest principles and progressive concern for social advancement, but also a bold and courageous citizen who never put personal interests before those of the community. One example of this was when he left the University as a protest during student unrest.

He took the refusal to elect him as an active member of the Academy of Sciences as a public affront, since almost all the Universities and learned societies in Russia and a number in other countries had elected him as an honorary member, and expressed their angry indignation at this rebuff.

It is instructive to recall that, despite the deep friendship between Mendeleev and Butlerov, when they were involved in their well-known controversy about the existence of spiritualism Mendeleev spent much effort and time in attempting to refute Butlerov's errors and misconceptions by experimental and strictly scientific means—with objectivity, loyalty to principles and love of truth which never deserted them.

The Society reacted vigorously more than once to the reactionary actions of the Tsarist government. Below is a characteristic excerpt from the minutes of the meeting of the Chemical Section of the Russian Physico-Chemical Society, four days after the infamous mass shooting of the workers in the Palace Square on 9th January 1905. The minutes, signed by N. S. Kurnakov, say: "In view of the terrible events of recent days and the impossibility of finding the peace of mind needed for the discussion of scientific reports, the Chemical Section, on the suggestion of the Council, resolved to close the meeting... The memory of those who fell was honoured by standing". Several subsequent meetings of the Society were also overshadowed by the political events of those times.

On 9th January, Mendeleev, troubled by the atrocities in the streets, went to see S. Yu. Vitte, in an attempt to persuade him to stop the massacre, but returned extremely depressed, since it was all to no avail[10].

The Society not infrequently approached the Tsarist government with requests and proposals concerning improvement of higher chemical education, greater autonomy for the Universities, admission of women to Universities, financial aid for research and other questions, but these were almost always rejected.

During the First World War, when the whole Russian industry, including the chemical, stood revealed in all its enormous backwardness, being unable to meet the needs of

defence and the production of essential medical supplies, the chemical community showed great initiative and persistence, and obtained permission to extend the scope of the most nationally-important scientific investigations.

Russian chemists throughout the last century devoted much time and effort to the popularisation of chemistry. Popular scientific lectures were often given by Hess, Butlerov, Il'enkov, Kittary, Khodnev, Sokolov, Markovnikov, Lesgaft, Shugaev, Shilov and Kablukov; these lectures were a great success. The Society took part in several exhibitions, where new synthetic compounds and apparatus, created with the Society's help, were demonstrated.

The Moscow Polytechnical Museum was founded in 1872, chiefly through the efforts of Professors Bogdanov and Arkhipov of Moscow University, and the Moscow Society of the Friends of Natural Sciences, Anthropology and Ethnography§. A number of exhibits was given to the Museum by members of the Russian Physico-Chemical Society, who gave popular lectures at the Museum.

It is clear from the above that the pre-revolutionary development of the Society was often chequered. It may be interesting to recall that among those professors and lecturers who left Moscow University as a sign of protest against the actions of the Tsarist Minister Kasso were such prominent members of the Chemistry Department as V. I. Vernadskii, N. D. Zelinskii, A. V. Rakovskii, N. A. Shilov, A. E. Chichibabin, S. S. Nametkin, A. K. Reformatskii and many others. The Chemistry Department noted in its records the enormous loss suffered by the University as the result of this action and in appreciating the immense sacrifice made by the people concerned, it expressed to them its deep sympathy and certainty that "in any case their gifts would not be lost to science, which is close to us all". Vengeful Tsarist officials stooped so low as to forbid the Russian Physico-Chemical Society twice to make a collection towards a monument to A. M. Butlerov in Kazan.

Mendeleev and Menshutkin died in January 1907. These grievous losses naturally led to an even stronger wish to consolidate the "chemical fraternity" (Mendeleev's expression), and the special meeting of the Russian Physico-Chemical Society dedicated to Mendeleev's memory and held in March 1907 adopted the resolution to organise periodically Mendeleev Congresses of Pure and Applied Chemistry¶. The First Mendeleev Congress took place in December 1907 in St. Petersburg; it united not only chemists but also physicists, engineers, technologists and a number of biologists. For this reason, the Chairman of the Congress was the eminent chemist N. N. Beketov; the Praesidium of the Congress included, as Vice-Chairman, P. N. Lebedev, the physicist; N. E. Zhukovskii, the mechanical engineer; I. A. Kablukov, S. N. Reformatskii, F. M. Flavitskii and P. I. Valden, the chemists; D. N. Pryanishnikov, the chemist and agricultural chemist; the Swedish chemist Arrhenius, and as Secretaries—L. A. Chugaev and K. P. Kasterin.

The First Mendeleev Congress was very representative and fruitful. Over a thousand delegates from 80 cities took part in it. All the most eminent Russian chemists, physicists, and technologists played an active part in the work of the Congress.

The Second Mendeleev Congress took place in St. Petersburg in December 1911. It was concerned not only with questions of general chemistry and physics, but also with chemico-technological, metallurgical, silicate, pharmaceutical and food problems. N. A. Umov was Chairman of the Congress, N. D. Zelinskii, T. A. Tamman, D. A. Goldgammer and A. G. Gruzintsev were Vice-Chairmen, and L. V. Pisarzhevskii and A. F. Kolli—Secretaries.

Foreign scientists attended the Congresses. During the Second Congress the Mendeleev Museum, situated in part of his University flat, was opened at St. Petersburg University. This is not merely a commemorative institution, but also a scientific one, since it contains Mendeleev's collected manuscripts and published works, which are still being studied and republished†.

The fact that no funds were made available to establish a Chair of Physical Chemistry at St. Petersburg University was lampooned in a specially written satirical play by B. B. Byzov and colleagues "A Tragedy of Physical Chemistry or the Fatal Hole in the University Stocking", which was performed at the Second Congress.

Further Mendeleev Congresses took place after the October Revolution.

THE SECOND FIFTY YEARS

The October Socialist Revolution, which turned the history of mankind in a new enlightened direction, naturally also had a revivifying effect on the chemical community. Scientific life, like the life of any organism which is bound up with its environment—climate, sources of nutrition and other vital conditions—is bound up with the social structure, the ideological interests of the society, its economic possibilities and aims, its cultural level, etc.

Thus the second fifty years of the Society's activities are characterised not only by an approximately 300-fold growth of its membership, but also a sharp change in the content and form of its work. Whereas formerly most of the members were science teachers predominantly from capital and large cities, after the Revolution there has been an ever growing influx into the Society's membership of specialists in chemical and allied industries, as well as industrial innovators and students, working in all the chemical centres of the Soviet Union.

At present the Mendeleev Society consists of 1949 primary organisations, 81 Republican, area and regional associations and a total of 171,000 members. The membership of the Russian Physico-Chemical Society in 1917 totalled 565.

In addition to the many specialised sections, the Society has under its aegis many teams working on special projects, and various commissions, institutes, laboratories, courses, schools, groups—with numerous annual cycles of lectures and practical courses for raising scientific and technical qualifications, excursions to leading industrial concerns and research Institutes both in the Soviet Union and in other countries, predominantly the Socialist ones. Participation of students and pupils from the higher forms of high schools has recently increased considerably—the "Young Chemist" section of the Society, organised 3 years ago, now has a

§ In response to public requests, the Government together with industrialists assigned 500,000 roubles towards the establishment of the Museum. A special building was built for the Museum in 1877; it now belongs to the All-Union Society "Nauka" (Science).

¶ These Congresses are now known as the Mendeleev Congresses of General and Applied Chemistry.

† In connection with the forthcoming centenary (in 1969) of the discovery of the Periodic Law, the Government has decided to place the whole of Mendeleev's flat at the disposal of the Museum and to refurbish it. The Leningrad section of the All-Union Chemical Society organises annual Mendeleev readings, devoted to present day chemical problems.

membership of 75 thousand. The All-Union Chemical Society, together with the "Nauka" Society, organises chemical contests and exhibitions and publishes popular scientific literature. The Mendeleev Society organises hundreds of scientific and technological meetings and conferences in various towns and factories every year.

The Mendeleev Congresses of Pure and Applied Chemistry enjoy great popularity in the Soviet Union and abroad; they are milestones in chemical circles, attracting thousands of active participants in recent years. Each Congress has been carefully prepared and has served not only as a review of achievements, but also as a gateway to new and fruitful lines of research and progress.

The Third Congress, convened in 1922 in Moscow (the first after the October Revolution) paid particular attention to the development of the chemical industry, which at that time was going through a difficult period of recovery.

The Fourth Congress took place in 1925, in Moscow; a number of fundamental theoretical studies in chemistry, physics and biology were reported, as well as communications concerning new chemical technological investigations.

The Fifth Congress took place in 1928, in Kazan—"the Russian chemical Mecca"‡; it was dedicated to the memory of A. M. Butlerov and his scientific legacy. In addition to the theoretical papers, the Congress approved unanimously a note on the application of chemistry to the national economy submitted not long previously to the Government, and adopted a number of resolutions aimed at the construction of chemical plants and the application of chemistry to agriculture on a new scientific and technological basis. This Congress initiated the All-Union Bureau of Higher Chemical Education, the Commission for the Chemical Nomenclature of Inorganic Compounds, and expressed a wish to establish a chemical research Institute in Kazan, which was created under the directorship of A. E. Arbuzov and has been for many years now active in much original work.

The Sixth Mendeleev Congress was held in 1932 in Kharkov, during the final period of the First Five-Year Plan; it was planned to coincide with the fifteenth anniversary of the October Revolution. At this Congress it was possible to summarise the significant achievements of Soviet Chemistry during the early years of the First Five-Year Plan and to outline new perspectives for the Second Five-Year Plan. The Congress looked particularly closely at the problems of further development of the main branches of the chemical industry—the production of sulphuric acid, synthetic ammonia, phosphorus and potassium fertilisers, the development of electrochemical industries, the production of artificial fibres, plastics, and synthetic rubber, as well as the training of chemists and the various aims of applying chemistry to the national economy. This Congress adopted the resolution concerning the need for uniting the chemists working in different areas of science and technology within the single Mendeleev All-Union Chemical Society.

The Seventh Congress took place in 1934 in Leningrad and celebrated the centenary of Mendeleev's birth. Many foreign scientists attended this Congress. The main papers dealt with the modern status of the Periodic Law and Mendeleev's other fundamental work in various spheres of science and technology, and the current problems in these directions.

The Eighth Congress was held in Moscow in 1939 and was the best attended and most representative of all the others. Hundreds of the most diverse papers were given in plenary and specialised sessions, which reflected the considerable achievements in theoretical and industrial research; the main goals of chemistry within the National Seven-Year Economic Plan were also considered. Foreign scientists contributed many papers at this Congress§.

The war which broke out in 1941 delayed the Ninth Congress by many years, in fact until 1965. This Congress, unlike its predecessors, dealt with narrower, more current problems linking chemistry with biology and the corresponding areas of technology: the application of chemistry to agriculture, medicine and the production of food. It took place in Kiev. The Congress discussed fertilisers, animal feedstuffs and sanitary preparations, chemicals for the protection of plants, pharmaceutical preparations, perspectives in synthetic foodstuffs, and many other problems.

The Tenth Mendeleev Congress will take place in the autumn of 1969 in Leningrad, and will celebrate the centenary of the Periodic Law, and deal with its status, applications and perspectives.

The connections between the Society and various Ministries and scientific and economic organisations are growing closer every year.

Many books[12,13] and articles[14-38] dealing with the achievements of Soviet chemistry during the last half-century were published in connection with the Jubilee of the October Revolution in 1967. We shall be dealing later with the Society's work at various periods of Socialist progress. Together with the development of well-established schools, many new schools of chemistry and many new lines of research appeared in the Soviet Union, some of which have gained world recognition, and are developing vigorously not only in the direction of chemical science and industry, but also in close contact with physics, biology, geology and other natural and technological sciences. The new Soviet schools of chemical kinetics and catalysis, photochemistry, electrochemistry, polymer chemistry, fundamental organic synthesis and organo-elemental chemistry, naturally occurring compounds, radiochemistry and isotopes, physicochemical mechanics, and others, are well known.

"Hybrid" sciences have appeared and are rapidly developing: among them chemical physics, biochemistry and agricultural chemistry, bio-organic chemistry, molecular biology, polymer chemistry, radiochemistry, geochemistry and biogeochemistry, photochemistry, chemotherapy, chemical microbiology, astrochemistry and cosmochemistry, chemical materials science, chemical cybernetics.

Schools of chemistry and research have been developing, since the Revolution, in all Soviet Republics and regions, in industry, farming, clinics, expeditions on land, sea and in space.

It is relevant to recall that before the Revolution there were no national organisations coordinating and directing the development of chemistry; there were only small groups of qualified chemists working in the Academy of Sciences, colleges and factories. There was not a single Chemical Research Institute. Therefore the Russian Physico-Chemical Society, whose active members included practically all the leading and most highly qualified chemists in the country, rapidly became the most authoritative scientific association of chemists not only in Russia, but also abroad. Mendeleev, in his remarkable note, only published in 1966, "What kind of Academy is needed in Russia?"[39] stressed the need for the integration of science

‡ A. E. Favorskii's expression.

§ Detailed information about the work of all the Mendeleev Congresses is available in the Transactions; that of the first eight is described in V. V. Kozlov's monumental work[11].

and technology and the importance of the Academy of Sciences as a social factor. He said:

"The monastery, the academy and the university—these are the successive stages of the development of science, characteristic of past centuries... It could be said that the rôle of the monastery in science was first progressive and then conservative. In the most recent times.... science made a further step, directly into life itself. Almost every Ministry needs a scientific committee...where possible mutual contacts have been established, and scientific societies formed....

The history of the development of Russian scientific societies is short, but it is already very instructive.... by summation of resources achieving a more significant resultant... Without taking into account the development of scientific Societies in our country it seems to me impossible to achieve any further understanding of the rôle of the Academy of Sciences. Science is absolutely free. That is how it has come to be in scientific societies... The Academy will have dual responsibilities: firstly, as a central scientific society... secondly as a central scientific council, which should also deal with undertakings of practical national importance.

....Science is pre-eminently not a private and detached concern, but a social and public one....

...The Academy should have the funds not only for its own research programmes but also for helping other societies in this respect..."

Much of what Mendeleev was urging only came to be realised after the Revolution.

The qualitative and quantitative growth of chemical science and technology in the USSR has, undoubtedly, been determined to a great extent by the industrialisation of the country and the genuine cultural revolution which has been, and is being, promulgated by the Communist Party since the first days of the October Revolution. In fifty years Soviet chemistry has grown into a mighty power, which at present produces about fifteen thousand various products in amounts several hundred-fold greater than before the revolution. As early as December 1917 a chemical section was established within the Supreme National Economic Council, in which highly qualified chemists with a social awareness played the most active role, under the direction of L.A.Karpov. Lenin, in his article "Current Aims of the Soviet Government" put the development of the chemical industry among the top-priority aims, and in his "Outline Plan for Scientific and Technical Developments" he said: "The Academy of Sciences, having started a systematic investigation and survey of the productive potential of Russia, should be commissioned forthwith by the Supreme National Economic Council to form a series of specialist commissions to expedite as rapidly as possible a plan for the reorganisation of industry and the economic progress of Russia"[40].

The Russian chemical community, represented by the most outstanding scientists such as L. Ya. Karpov, A. N. Bakh, V. N. Ipat'ev, E. V. Britske, P. M. Luk'yanov, Ya. V. Samoilov, D. N. Pryanishnikov, N. S. Kurnakov, N. D. Zelinskii, N. F. Yushkevich, V. P. Kamzolkin, V. S. Kiselev, M. N. Gurvich, I. A. Tishchenko, B. S. Shvetsov, P. P. Budnikov and others, came out on the side of the Soviet government at once, without vacillation.

The enthusiasm and deep sense of responsibility to their country felt by Soviet chemists is well illustrated by the now historical note, sent by a considerable group of scientists to the Soviet Government in March 1928, offering their services to the development of chemical science and technology, and the use of their achievements in other areas of the national economy and culture. These proposals were discussed with a delegation of scientists¶ and considered by a specially appointed Government Commission, made up by Ya. E. Rudzutak, G. K. Ordzhonikidze, A. I. Mikoyan, G. M. Krzhizhanovskii and N. P. Gorbunov; as the result of this, the Council of the People's Commissars of the USSR issued an edict on 28th April 1928 "Measures for the Application of Chemistry to the National Economy", which was followed by the formation of a very representative Committee of highly qualified specialists and Government officials, and the organisation of a chemical section in the State Planning Organisation of the USSR. The Committee was chaired by Ya. E. Rudzutak, and then by V. V. Kuibyshev.

The remarkable note mentioned above, which even now makes most interesting reading, said:

"..... The profound changes which have recently occurred in the concepts of the elementary nature of matter mark an epoch in the history of science. In the field of chemistry the past decade has seen attempts at penetrating the structure of matter, which open up limitless future possibilities of its technological exploitation (catalysis, radioactivity, intra-atomic energy, etc.). The achievements of theoretical chemists have created such an integrated picture of the interaction of atoms that it has become possible to elaborate systematically and rationally an experimental elucidation of, among others, the chemical processes in the soil and in plants. Chemistry is now at the point of transition to the most extensive and profound development of all its technology.

The new chemistry has created a large number of materials until recently completely unknown, such as synthetic fibres, oil, leather, rubber, plastics, tanning substances, light alloys, etc., and its further development is bound to create a revolution in the industrial economy. Even greater economic achievements are foreshadowed by the use of all wastes, i.e. raw materials present in the wrong place which have so far not found their application.

A general plan of economic development must take into account all the prospective developments of modern science, which clearly show the ever growing influence of chemistry on the replacement of many mechanical processes in industry, agriculture, defence and daily life by chemico-technological ones.

A great advantage for the creation of future new technology in the Soviet Union is likely to be, paradoxically enough, its very poverty at this time, i.e. the absence of large investments in the form of capital and equipment, since experience has shown that the application of advanced scientific ideas is often hampered in capitalist countries by the need to run the equipment down to complete depreciation.

These measures designed to advance chemistry can effect the most radical changes both in the technological aspect and the economic structure of industry, be it metallurgy, mechanical engineering, mining, transport, textiles and other branches of the national economy, considerably lowering the costs of production and raising the efficiency of capital investment.

The solution of the above economic problems is particularly bound up with the development of chemical science in the USSR.

¶ The delegation was led by A. N. Bakh, who later became the first President of the Mendeleev All-Union Chemical Society.

The Soviet Union, as a country which has taken giant steps in the rearrangement of the social and economic conditions must first of all direct the full might of chemical thought towards the fullest development of chemical technology. This will give a firm basis for economic development and at the same time ensure the country's invulnerability and independence in the event of possible hostile actions.

History has shown that the rapid flowering of chemistry in the nineteenth century, which created all the brilliance of chemical science seen now, was initiated and determined by theoretical scientists: Lavoisier, Brane, Dalton, Faraday, Dumas, Le Chatelier, Frankland, Hoffmann, Bayer, Clapeyron, Zinin, Mendeleev, Butlerov, and others. Lavoisier, Faraday, Lomonosov and Mendeleev examplify the fact that the greater the scientist as a theorist, the clearer his view of the requirements conditioned by life and by technology.

In order to utilise rationally the country's immense and varied natural resources it will be inevitably essential to solve a series of new problems on the basis of our own, original, creative and purely scientific work. It is not sufficient to make use of Western discoveries—we must ourselves be at the forefront of chemical research.

It follows from this that our country's urgent aim should be the widest development of scientific research, regardless of cost, and not only in applied but also in theoretical chemistry.

In addition to extensive planned research related to current industrial needs, generous funds should be allocated to theoretical research outside such a plan, which would provide starting points for radical changes in chemical technology.

It is essential to extend and reinforce mutual contact between our scientists and industrial organisations and the leading countries of the world, making these contacts more constantly systematic and easy, by increasing the number of visits to foreign countries, by inviting foreign consultants to the USSR, and by other means.

Scientists should be involved in the development of a general plan for the chemical industry and agriculture, and play a bigger part in the work of factory laboratories and industrial workshops.

Great care must be given to the organisation and equipment of factory laboratories, and to improving the working conditions of factory technical personnel, always providing opportunities for improving their qualifications.

The call to organised work embracing such wide horizons will, naturally, bring to life the potential creative forces and enthusiasm in both the mature and the young chemists, physicists and technologists.

The undersigned appeal to the Government to organise within the Soviet People's Committee a special Commission on the application of chemistry to the national economy, to discover and apply all the measures necessary for achieving this goal"[41].

The Soviet People's Committee defined the main aims of the Commission as follows:

"The Commission must give top priority to a detailed scientific, technological and economic study of the following problems: the rational utilisation and extension of native natural resources; the application of modern chemical developments to individual branches of industry and social needs—building, transport, public health, and others; the production of agricultural fertilisers and insecticides and fungicides; the establishment of a potash industry; the further development of the organic dye-stuffs industry; the radical reconstruction of the coke and petroleum industry; the industrialisation of modern forest chemistry; the investigation and maximal development of the rare elements industry; the basic problems of modern synthetic chemistry (synthetic rubber, petrol and liquid fuels, synthetic esters, etc.); and the increased production of chemically pure reagents and laboratory equipment in the USSR"†.

The penetration of chemistry, its methods and products, into the different areas of the national economy became so important and widespread that a special term "chemisation" was coined for it in the Soviet Union, later used also in other countries; it has come into common usage in much the same way as "mechanisation" and "electrification".

During the First Five-Year Plan vast deposits of Khibinsk apatites, and Solikamsk potassium salts were discovered and developed; the first synthetic ammonia plants were built and a series of other basic mineral and organic chemical concerns established. Large teams began working within a single plan, in a coordinated tackling of research, design, construction, equipment and production. The chemists and engineers showed great creative enthusiasm in those years, helping in a variety of ways to solve the difficult problems of prospecting for and utilising mineral deposits, and to apply scientific discoveries to practical needs.

Members of the Society initiated the establishment of a series of Institutes, both in central and remote regions. They now number over 150.

A group of organic chemists led by I. P. Losev prepared the first comprehensive report on the paths for the development of basic organic chemical industry, which was approved by the planning bodies.

During the Second World War the Society carried out diverse research and production projects for defence. Many leading specialists offered their help to the Government in the very first days of the war; as the result of this, the State Committee for Defence appointed an executive to deal with chemical matters, with a staff of specialists who helped to mobilise those working in colleges, research, and industrial organisations for development work required to meet the needs both of the frontline and the rear. Much was achieved in mobilising natural resources and raw materials, organising the production of sanitary and medicinal preparations, and in matters of chemical defence.

Whereas the role of chemists in the early Five-Year Plans was primarily consultative, on their own initiative, and concerned with individual proposals, after the war the All-Union Chemical Society has been organically and systematically included within the general State economic planning; this has occurred in accordance with Party and Government resolutions. The Society now not only puts forward its proposals and criticisms but also makes practical contributions towards the realisation of plans, the improvement of the quality and tempo of research, of design and construction projects and of building and industrial undertakings. This activity of the Society is continually growing and gaining in variety, especially on sites.

In recent years much work has been done by the Society's sections dealing with higher education, polymers, silicates, and the application of chemistry to agriculture (chiefly in the South-Western regions).

Evaluation commissions, reviewing and recording many hundreds of research and industrial papers, have been

† Detailed data on this are in the Transactions of the Commission's plenary sessions and also in the Journal published by the Commission "Khimiya isotsialisticheskoe Khozyaistvo" (Chemistry and Socialist Economy) (Gosudarstvennoe Nauchno-Tekhnicheskoe Izdatelstvo).

working hard both at headquarters and in some of the branches. The Society acts as scientific and technical consultants in many industrial concerns. The State Committee of Science and Technology at the Council of Ministers of the USSR, the Academy of Sciences of the USSR, and the Trade Unions maintain regular contact with the Society, to mutual advantage. The Society aims not only at responding creatively to various Party and Government resolutions, but also at initiating and promoting progressive ideas, techniques, and theoretical and practical achievements.

Special mention should be made of the Society's work over many years in organising systematic courses, conferences and reference publications on the chemistry and technology of polymers, which are very popular among chemists for bringing them up to date. Some sections of the Society have done similar work on new analytical techniques and production control. The Society also has considerable consultative functions in connection with the current economic reforms. However, these progressive functions are concerned more with chemico-technological and industrial matters, than with theoretical and scientific ones. Therefore the Society is now assisting with the development of fundamental research both in Institutes and in industrial laboratories.

Among the most active leading members of long standing in the Society during the Soviet era have been: N. S. Kurnakov, N. D. Zelinskii, V. M. Rodionov, V. S. Kiselev, I. P. Losev, P. P. Budnikov, P. M. Luk'yanov, A. I. Lazarev, V. V. Kozlov, Z. A. Rogovin, S. N. Danilov, S. A. Shchukarev, A. I. Brodskii, M. M. Dubinin, A. E. Porai-Koshits, L. K. Lepin, E. A. Shilov, I. I. Chernyaev, S. S. Nametkin, N. M. Zhavoronkov, O. E. Songina, V. M. Kakabadze, O. S. Stepanova, N. M. Karavaev, S. V. Gorbachev, and other chemists.

We shall now mention some achievements in those spheres of modern Soviet chemistry where the main contributions have been made by active members of the Society.

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The variety of chemical elements and natural raw materials used by chemical industries increases annually. Petroleum, industrial and natural gases, coal, wood pulp, sand, limestone, clay, aluminosilicates and many other widely distributed natural raw materials are extensively utilised. The scope of synthetic chemistry has grown tremendously.

The advances of atomic physics and chemistry have made it possible to synthesise and to degrade elements, thus laying the foundation of revolutionary transformations in chemistry and in chemical technology. The remarkable words of A. M. Butlerov, written about ninety years ago, are relevant to the immense and rapidly expanding advances in organic synthesis. He wrote: "... it is certain that every organic substance can be synthetically produced"[42].

These words have become the slogan of modern chemistry, whose aim it is to synthesize the most varied and complex substances with tailor-made properties, utilizing for this purpose common and preferably cheap raw materials. At the same time there has been a great increase in the utilization of mineral raw materials containing rare and transition elements, coloured and noble metals, etc. Chemists are paying more and more attention to complex processing methods and to the elimination of industrial waste.

The problem facing contemporary science is extremely important and difficult: the relationship between the properties of numerous and varied materials and substances and their composition and structure. Many of these substances are novel and important, including semi-conductors, thermostable materials, quantum-generating and biologically active substances.

The deep penetration of organic chemistry into biology has led to the most refined and complicated syntheses of analogues of natural products—e.g. sex hormones, vitamins, enzymes, antibiotics, etc.—and to the discovery of substances carrying genetic information and of mutagens, thus demonstrating the great achievements of science. Similarly, the collaboration of physicists and chemists has resulted in the discovery of twelve elements of the periodic system (eleven transuranium elements) and over 1800 radioactive and stable isotopes. Many of these have proved useful in various spheres of industry, public health and scientific investigations. The achievements of inorganic chemistry have been enormous in the last twenty-five years, especially in radiochemistry, the chemistry of rare and transition elements, extra pure semiconductors, ultra hard and chemically stable substances, etc., as well as in studies in depth of the structure, properties and transformations of inorganic matter. Many of the rare and transition elements have remarkable properties and play an important part in the production of special steels and metal alloys, endowing them with hardness, thermostability, resistance to corrosion and many other valuable properties. Certain rare elements are widely used in electronics, in radio engineering, photographic technology, production of ignition compounds, in medicine and in agriculture. Compounds of some chemical elements are used as microfertilizers and in food supplements in animal husbandry, etc.

As a result of notable achievements in organic syntheses, various classes and groups of organic compounds previosuly regarded as strictly individual have become interconvertible, and some considered inactive ("chemical corpses" in the acute words of M. I. Konovalov) are now easily converted into other compounds. These successes have opened up possibilities of using less valuable, extensively occurring raw materials instead of more valuable and scarce ones. The raw material resources of chemical industry are thus constantly expanding.

On the basis of extensive creative efforts of Soviet chemists the petroleum and gas industries have created numerous new processes which form a solid foundation for basic and heavy industrial organic synthesis.

The production of high molecular weight compounds has developed extensively and fruitfully, particularly since the plenary session of the Central Committee of the Communist Party of the USSR in May, 1958. Soviet industry produces many scores of various types of rubber, plastics, fibres, films, etc. Many synthetic high-molecular weight compounds have remarkable properties superior to those of natural products. The achievements in this area have resulted in a peculiar competition between the synthetic and natural materials.

The notable work of S. V. Lebedev and other chemists has resulted in the Soviet industry's being the first in the world to produce synthetic rubber from alcohol. The method of Lebedev has found wide application in several countries abroad. Synthetic rubber is also made in the USSR from other raw materials, e.g. gases from petroleum processing, acetylene, etc.

Work on the synthesis of organosilicates has acquired great interest and increasing importance since their use in the production of rubber-like plastics results in great sta-

bility to temperature variations, and in electrical insulation, hydrophobic and other properties. They are also used in making special high quality resins, lacquers, etc.

Soviet workers have synthesised and studied in detail a series of new and modified synthetic fibres of high quality, used in many branches of technology.

Considerable advances have also been made in recent years in the production of inorganic polymers of high thermostability, particularly among polyphosphates and polysilicates.

High molecular weight ion exchange resins capable of removing various ions from solutions are widely used in many technological processes which require the isolation of rare, valuable or radioactive elements from very dilute solutions. The resins are also used in the high purification of water, in analysis and in other spheres. Soviet chemists have synthesized scores of divers highly efficient ion exchange agents.

Among the outstanding achievements of Soviet organic chemists over the last 20–30 years the following should be mentioned as having theoretical and practical significance: dehydrocyclization of paraffins to cyclopentane hydrocarbons; the development of the cumene process of phenol synthesis and the synthesis of acetone from isopropylbenzene; the development of the synthesis of benzene homologues; the discovery of the disproportionation reaction of cyclopentane in the presence of vanadium oxide; the discovery of the opening of three-membered rings through the action of mercury acetate; the development of processes for the production of alcohols and fatty acids through the continuous oxidation of paraffins, etc.

Of great future significance are the numerous studies in various spheres of organo-elemental chemistry. Among these especially noteworthy are the development of the diazo methods of synthesis, the investigations of ferrocene, and the study of the reactions of radicals in solution.

A series of new methods of preparation of aromatic compounds has been developed. A method for the production of anthraquinone sulphonic acid has been worked out; interesting studies of the chemistry of heterocyclic compounds have been carried out. A new area of organic chemistry—fluoro-organic compounds—has been developed. V. M. Rodionov has worked out original methods of synthesizing beta-amino acids. V. E. Tishchenko has studied in depth pinene and camphene, whilst A. E. Arbuzov has investigated terpenes.

A. E. Favorskii and his school have produced extensive and very fruitful work in the field of organic syntheses based on acetylene, including the production of synthetic rubbers, glues and other high-polymer materials.

One of the most important problems facing chemical industries is the substitution of synthetic raw materials for edible plant raw materials currently used for technological purposes.

Considerable successes have been achieved in the syntheses of new and of more effective medicinal, disinfectant and analgesic compounds. Soviet medicine is indebted to I. N. Nazarov for the discovery of promedol and of other very effective analgesics. Substances enhancing the maturation of blood corpuscles, organic fluoro-compounds and other polymers are used successfully in surgery in replacements of blood vessels, and of bone and other tissues.

A. E. Chichibabin, V. M. Rodionov, their students and collaborators and other investigators have carried out detailed investigations into drugs and into series of analogues of natural products. Recent years have seen successful collaboration between chemists and biologists and doctors on the synthesis of powerful agents against tuberculosis, pneumonia, encephalitis, dysentery, poliomyelitis, leukemia and various infectious diseases.

Numerous chemicals have been developed which are active against plant pests and diseases and against weeds; defoliating and desiccating agents for the pre-harvest removal of leaves from cotton plants, potatoes and other vegetables; stimulants and regulators of plant growth and many other physiologically active substances. Herbicides and scores of pesticides as well as defoliants (particularly in cotton cultivation) are widely used in agriculture.

A. E. and B. A. Arbuzov, in Kazan', have carried out basic research into the synthesis of organo-phosphorus compounds and of medicinal substances. It is noteworthy that these studies which have great practical importance resulted from purely theoretical investigations by A. E. Arbuzov into the various aspects of a new class of compounds, viz. esters of phosphoric acids. Many agricultural toxic chemicals which have found extensive application were synthesized by workers of the Institutes of the Academy of Sciences, at the Scientific Fertiliser and Insectofungicide Institute (NIUIF), the All-Union Institute for the Chemical Protection of Plants (VNIIKhZR) and others. Institutes in Moscow, Kazan', Kiev and other towns have produced extremely valuable work on the synthesis of organo-phosphorus insecticides and other producs.

Important original work on the synthesis of dye-stuffs, photoreagents for colour cine-film and various fine chemicals has been done by M. A. Il'inskii, A. E. and B. A. Porai-Koshits, N. M. Kizhner, A. I. Kiprianov, N. N. Vorozhtsov and others. The remarkable theoretical work of A. N. Terenin in photochemistry should be mentioned. The study and synthesis of organo-elemental compounds has greatly expanded in the Soviet Union. Among these compounds many are effective agricultural agents, intermediates in the production of polymers, etc. The Institute of Organo-elemental Compounds of the Academy of Sciences of the USSR was established for the extensive development of studies of these compounds because of their theoretical and practical significance.

Considerable achievements in inorganic chemistry have resulted in recent years from the work of I. I. Chernyaev, A. A. Grinberg, A. F. Kapustinskii, S. A. Shchukarev, V. G. Khlopin, E. V. Britske, N. F. Yushkevich, G. G. Urazov, B. A. Nikitin and others.

Outstanding achievements must be noted in inorganic materials science, which have ensured the production of various compounds for atomic, nuclear and electronic technology. These achievements were preceded by an enormous amount of original work on the isolation of rare and radioactive elements and their isotopes. Many of these are isolated in the so-called spectroscopically pure state (this degree of purity allows the presence of one atom of admixture to 10^8–10^{12} atoms of substance).

Numerous new metal alloys, glass, ceramic and other materials have been created, possessing previously unattainable stability, hardness, thermostability and resistance to radiation and various chemical actions (e.g. corrosion). Soviet industry is now producing a whole series of valuable types of glass, glass fibres, thermo- and electro-insulating materials. The development of silicate chemistry owes much to the work of I. V. Grebenshchikov, P. P. Budnikov, I. I. Kitaigorodskii, N. A. Toropov and many workers in the building materials industry.

The achievements of Soviet chemistry have also been great in the theory of complex compounds and in the development of new methods of production and refining of the platinum group of metals, viz. rhodium, iridium, osmium, ruthenium, etc.

The chemistry of rare and radioactive elements has been widely studied, entailing the development of many novel, refined methods of investigation, of isolation, separation and profound purification of substances. Whilst in the years immediately following the October Revolution main efforts were directed to the development of methods of isolation of radium from ores and to the utilization of certain rare metals in metallurgy, in recent years the creation of atomic technology has resulted in extensive original work on the chemistry and technology of uranium, thorium and other transuranium radioactive elements, as well as beryllium, zirconium and others.

The rapid development of the production of semiconductors has led to divers studies and investigations in depth of substances possessing electronic conductivity whose magnitude places them midway between metals and insulators. With this aim in view, various sources of raw materials have been investigated as well as methods for obtaining such elements as germanium, silicon, indium, tellurium and others in a pure state, and for preparing a whole series of their chemical compounds.

Contemporary aircraft equipped with jet engines and other new technological developments require the creation of novel types of metal construction, stable to high temperatures, pressures, corrosion and other influences. Chemists and metallurgists have succeeded in solving numerous difficult problems in utilizing for these purposes metals new to the industry—viz. magnesium, titanium, and various alloys containing rare elements.

Great contributions to radio- and isotope chemistry have been made by V. G. Khlopin, I. D. Bashilov, I. V. Kurchatov, G. N. Flerov, A. P. Vinogradov, I. E. Starik, A. I. Brodskii, V. I. Spitsin and others.

The successes of Soviet chemistry have resulted from profound theoretical studies, based to a considerable degree on the use of refined physical methods of investigation, i.e. spectroscopy, X-ray analysis, radioactive isotopes, mass-spectrometry, chromatography, polarography and many others. Much original theoretical and practical work in analytical chemistry has been done by Soviet chemists.

Thanks to the high precision and rapidity of the new analytical methods automatic control and regulation of continuous industrial processes has become possible. Modern achievements in the production of ultra pure substances, in nuclear and electronic technology, in many areas of biology, medicine and other branches of science and technology would be impossible without the new analytical methods incorporating chemical and physical methods with high standards of instrument technology.

Penetrating and varied studies of divers important chemical reactions have been carried out, as well as of methods of their acceleration by means of catalysts, high temperatures, high pressures and other "levers" influencing the course of reactions. Significant contributions to this sphere have been made by the eminent Soviet scientists N. D. Zelinskii, N. N. Semenov, A. A. Balandin, V. N. Ipat'ev, E. V. Britske, P. P. Fedot'ev and others. Studies on reaction rates have resulted in the intensification of some industrial processes and the development of new technological procedures. N. N. Semenov was awarded the Nobel prize for his outstanding contributions to chemical kinetics and chain reactions (the Nobel prize was simultaneously awarded to the eminent British chemist Cyril Hinshelwood for his studies of chemical reaction mechanisms). This sphere of science originated in the Soviet Union and has developed fruitfully there for over a quarter of a century: the leading centre for these studies is the Chemico-physical Institute of the Academy of Sciences of the USSR. Outstanding theoretical studies on the structure, reactivity and energetics of chemical reactions have been carried out during the period of Soviet rule.

In recent years penetrating and extensive studies have been initiated into the mechanisms of surface phenomena which play a large part in the accomplishment of many technological processes, e.g. gas absorption, flotational enrichment of ores, resistance of metals to corrosion, etc. This sphere has been well served by A. N. Frumkin, V. A. Kistyakovskii, P. A. Rebinder, N. A. Izgaryshev, G. V. Akimov and others.

The most difficult problem of mastering atomic and nuclear processes has been solved in a short period of time by collaborative efforts of physicists, chemists and technologists.

Soviet chemical engineers have achieved considerable successes in utilizing native mineral resources, including many types of raw materials containing coloured metals and rare elements, phosphorus, boron and various other ores (work of geologists and chemists including A. E. Fersman, I. M. Gubkin, Ya. V. Samoilov and others, as well as E. V. Britske, N. F. Yushkevich, I. P. Bardin and others); before the Revolution most of the mineral raw materials were imported into Russian from abroad.

The discovery 40 years ago by the Academy of Sciences expedition and the exploration by NIUIF beyond the Polar circle of the world-scale deposits of Khibin apatite-nephelite ores as well as the discovery before World War II of large deposits of phosphorite in Karatau (Southern Kazakhstan) and of other deposits, have led to the establishment of extensive phosphate fertiliser industries producing at present about 450 times more fertilisers than before the Revolution. Utilization of novel types of raw materials (volcanic apatites, nephelites, etc.) previously not used, demanded much original work by chemists, which has enabled Soviet chemical and metallurgical industries to produce from these materials scores of valuable products—phosphate fertilizers and salts, phosphorus, fluorine salts, aluminium, soda, potash, cement, glass, etc.

The discovery and exploration in 1926 of the largest in the world deposits of potassium salts in northern Urals (in the Solikamsk district), and then of further potassium deposits in various areas of the USSR, laid the foundation for an extensive industry producing potassium fertilizers, magnesium, bromine, rubidium and various salts. It is relevant to mention here the extensive studies of other natural salts, based on their chemico-physical analysis (marine and lake sulphates, soda, borates, etc.), carried out by N. S. Kurnakov, G. G. Urazov, V. P. Il'inskii, E. V. Burkser, N. N. Efremov and many others.

Abundance of food stuffs and of raw materials for light industry is ensured in the USSR by the organisation of extensive, advanced and rapidly growing industry based on fixed nitrogen, together with developments in the production of phosphorus and potassium fertilizers and of chemical agents for the protection of useful plants and animals and of feed-preserving and sanitary substances used in animal husbandry.

The so-called combustible minerals, viz. petroleum, coal, natural gases, turf, etc., as well as wood pulp, are more and more widely used not only as fuel but also as valuable chemical raw materials. Their processing is complex, using energo-chemical methods. Chemico-technological methods of processing underground mineral deposits in situ are being studied, including the possibilities of dissolving, melting or gasifying a series of salts and ores ("geotechnological" processes).

Technologists have worked out complex methods of processing natural raw materials which eliminate enormous losses of valuable components in the solid, liquid and gaseous industrial wastes. In recent years much work has been devoted to the acute and important problem of air and water polution—a growing problem related to the expansion of industry.

Since the Revolution the science and methods of chemical technology, i.e. the mass conversion of raw materials into useful products, have been transformed. The enormous problems of Socialist construction have revivified it. Before the Revolution this science was largely empirical, it developed in a chaotic manner in the rapacious interests of profit-making concerns. In the Soviet Union the development of chemical technology proceeds according to plan and expediently, based on the theory and progress of all branches of physico-chemical and technical sciences, in the interests of maximal satisfaction of the needs of society as a whole.

New sectors of chemical technology are growing rapidly in the USSR, e.g. studies of processes and of apparatus, physico-chemical bases of industrial processes, their optimization and programming, as well as the science of chemical materials and machine construction.

Valuable results have been obtained from theoretical studies of chemico-technological processes by Soviet chemical engineers, especially in the field of contact processes and apparatus, intensification of production and separation and purification of products.

Valuable forward-looking work has been done on the production of oxygen and its application in various areas of chemical and metallurgical industries, resulting in considerable intensification of some important production processes (I. P. Bardin, P. L. Kapitsa et al.).

The growth of research and planning in new chemical industries has been considerably influenced by developments of theories of similarities and by model processes and apparatus, and in recent years by mathematical and physical methods of planning experiments related to the problems of chemical cybernetics. The study of processes and apparatus are much indebted to I. A. Tishchenko, L. F. Fokin, K. F. Pavlov, A. G. Kasatkin and others.

Recent decades have seen a particularly deep penetration of chemical methods not only into physics but into biology including its applied branches, viz. medicine, horticulture, animal husbandry, microbiology both bacterial and viral, and into the food industry. The cross-fertilization of natural and technological sciences has so great an influence on the direction of chemical efforts penetrating all spheres of life, that there is already talk of the coming of the "age of biology" in which the main roles will be played presumably by biochemistry, physiology, bioorganic chemistry, molecular biology, chemical cytology and other hybrid sciences coupled with the widest possible application of the latest physical and mathematical methods of research. After all, the knowledge of life processes, of metabolism, growth, fertility, transmission of heredetary characteristics, the functioning of the nervous system, variation of micro- and macro-organisms, is still modest. Significant results have been obtained in certain intermittently advancing areas of experimental physiology and biochemistry. It is obvious that problems involved in the life sciences require the most sophisticated and complex chemical and physical research methods. Until comparatively recently chemists and biologists collaborated in expeditions, in descriptive, analytical and synthetic methods of investigating natural products (this must have given rise to the conventional and imprecise term "chemistry of natural products"; strictly speaking, mineral substances forming the earth's crust, water and air also form natural products). Chemists and biologists are faced with the need to study in depth the processes occurring in living organisms. Whilst quite recently research was directed towards the composition, structure and properties of protein ("bricks"—amino-acids, hydrocarbons, lipids, terpenes and other components of natural and technical products, in the last decades research has concentrated on vitamins, enzymes, hormones, antibiotics and other physiologically active substances including medicinal and agricultural products as well as other regulators of life processes, possessing genetic, mutagenic and toxicogenic functions. Industrial production of certain vitamins and medicinal substances has been established in the USSR on the basis of experience at home and abroad (including the work of A. E. Chichibabin, V. M. Rodionov, A. E. Arbuzov, M. M. Shemyakin, A. P. Orekhov, Kh. U. Usmanov and others).

In recent years Soviet chemists have achieved successes in the synthesis of a series of important protein-peptide substances, in the studies of muscular contraction mechanisms, of the conditions of enzyme action in amino-acid metabolism, of the basis of the bioactivity of the main types of proteins and peptides. Of great significance are the studies to clarify the mechanisms of the transmission of hereditary characteristics by means of investigating the structure of deoxyribonucleic acids, as well as of one of the most important messenger ribonucleic acids involved in the synthesis of the protein chain from amino-acids. Valuable pioneer work has been carried out in the USSR on the use of numerous chemical compounds selectively altering hereditary characteristics (mutagens). Methods have been worked out for obtaining male and female sex hormones from available raw materials and for the synthesis of other steroid hormones. Significant results have come from investigations by Soviet biochemists into the synthesis of vitamins produced industrially (at the present time vitamins A, B_1, B_2, B_6, C and others are being produced). Developments are taking place in studies of blood, and blood substitutes have been developed. Considerable achievements have been made in the synthesis of physiologically important carbohydrates and lipids. Chemists, biologists and doctors are collaborating in the search for effective preparations against malignant tumours, carcinomata, sarcomata, etc.

Research work is becoming more and more team-work and increasingly complex. The clear demarcation previously existing between inorganic and organic or inorganic and physical chemistry is becoming blurred in many areas. Theoretical, methodological and prospecting investigations are increasingly done by the combined forces of the Academies of Science, graduate schools, professional institutes and plant laboratories according to a common, agreed plan. Much of this work is stimulated by the competitions and discussions initiated by the Mendeleev Society.

PROSPECTS IN CHEMISTRY

Soviet chemists are faced with tremendous and exciting problems. Developments in the study of the theory of structure and of reactivity of chemical compounds, of kinetics and chemical reaction rates, of the course of nuclear processes are opening more and more prospects of directed synthesis and transformation of elements and of their compounds and of enhancing the possibility of regulating life processes of creating new materially valuable products.

In the coming decades energetics will presumably cease to be the limiting factor in the development of electrochemical, electrothermal and other energy requiring industrial processes. This view is based on the long experience of the construction and exploitation of large thermo- and hydroelectric power stations and on the considerable advances in recent years in the building and use of atomic power stations. It is therefore to be expected that the production and use of oxygen, hydrogen, nitrogen, chlorine, caustic alkali, light metals, silicon, phosphorus and other elements and their compounds will expand, making these substances more easily available and cheaper. Because of new resources and of new forms of energy new technological processes will come into being, and many of the existing ones will be radically changed. Processes taking place at high or super-high temperatures will be increasingly important not only in the chemical and metallurgical industries but in many other branches of technology (mining, building construction etc.). Processes at extremely low temperatures will also be developed. The use of medium and of high vacuum will be extended. Electromagnetic and electrostatic action, ionizing radiation, radiolysis, photolysis and other physical "levers" will speed up processes in the desired directions.

These developments will lead to numerous new processes, apparatus, chemical products and construction materials. Even now the world chemical industry produces tens of thousands of compounds, and their number is constantly and rapidly increasing. The number and variety of chemical products is limitless.

Soviet research laboratories produce annually many thousands of new chemical compounds, hundreds of which are then produced industrially. This progress may be likened to an avalanche; it is directed to the satisfaction of requirements in the national economy, public health, defence, culture and everyday life.

Chemical technology has up to the present studied and achieved syntheses, degradations and other transformation on the "molecular level"; in the future these processes will also be developed on the "atomic-nuclear level". Radioactive processes of transforming one element into another, already realizable, will in the future extend the raw material sources of elements deficient in the earth's crust. The chemistry of organo-elemental compounds is expanding rapidly.

Significant progress is to be expected in the biochemical and especially the microbiological industry, solving important problems in the sphere of food production, of medicine, etc.

Thanks to new sources of energy, and to chemical and mechanical advances, it will be possible to investigate and to extract mineral raw materials from great depths of our planet—tens of kilometres, or even deeper, down. These problems are only beginning to be studied (at present the deepest bores are 7–8 kilometres deep, the average diameter of the earth being 6510 kilometres). At the same time the problems of the extraction and processing of mineral raw material underground (by dissolving, melting out, gasification) will be tackled, similarly to the underground extraction of solutions of rock salt which are distributed to soda-producing plants, and to the melting of underground deposits of sulphur by means of steam (a method long used in Louisiana). In the first instance such methods of extraction could apply to water soluble salts, e.g. potassium (as has been done in recent years in Canada), magnesium and others, as well as to low-melting minerals or those decomposable at comparatively low temperatures.

Electrochemical sources of power will introduce radical changes into land, air and cosmic transport. In the USSR as well as in other countries vigorous research is being pursued which should provide in the near future powerful, economic and portable chemical sources of power, replacing in many processes the heavy accumulators and the usual fuels, e.g. kerosene, gasoline, compressed and liquefied gases, etc., and possibly competing in certain applications with atomic power generators.

There is no doubt of the importance of research into the processes of photosynthesis, which play so tremendous a part in life processes on Earth.

The number of chemical elements known at the present time is 104 (element 104 of the periodic system was discovered by I. V. Kurchatov and named "Kurchatovium" in his honour); approximately 1800 radioactive and stable isotopes are also known. The heavy elements series of the periodic system is expected to be considerably extended in the future.

Concurrently with the studies of physical, chemical, biological and technological properties of the elements, their use and novel application are being developed. Obviously the widest and most varied application will be found for those elements which are most abundant in the earth's crust, in water and in air. To this type of raw material belong sand, clay, limestone, gypsum, salts and other common mineral raw materials. Petroleum and natural gas are of especial interest in many parts of the world. The enormous deposits of coal have to be used on the largest possible scale in conjunction with the production of a wide assortment of chemicals, similarly to the petrochemical industry. This also applies to peat deposits. Much more attention should be paid to the chemical technology and diversified use of wood pulp—the most widely available and self-replacing natural raw material.

The chemistry of high-molecular weight compounds will be developed on the widest possible scale.

The threatening shortage of pure fresh water in certain areas will be eliminated by desalination and purification of sea water and of underground water by chemical, mechanical and physico-chemical means, including the utilisation of heat from atomic reactors and of helio-technology.

Industrial waste waters present an acute and complex problem which will require complex methods and means of elimination to be worked out by joint efforts of science and technology (as has been done in recent years in the USSR in connection with some important problems in this sphere).

There are large areas in the USSR where the soil is acid, saline or eroded—and these defects will have to be remedied to ensure effective agricultural development. A solution of these problems is liming of acid soils, and treatment with gypsum of solonetz and solonchak soils. These measures are to be extended. The struggle against wind and water erosion—present on a very large scale in places—will have to involve the collaboration of chemists, physicists and soil scientists. A number of polymers, latex-like substances, silicates, etc. capable of binding and strengthening soil particles has already been investigated. But the economic aspects of this problem are not yet solved: they have attracted insufficient efforts and expenditure so far.

In the coming decades the plant foodstuffs will not be basically replaced, but will be enriched and supplemented by synthetic products (protein concentrates, amino-acids, carbamide, phosphates, microelements, vitamins, etc.).

Some food and feed production problems have, however, already been solved by synthetic chemistry, by-passing

crop raising, and this process will undoubtedly develop further.

The three sources of plant nutrition—nitrogen, phosphorus and potassium—are found in nature in widely differing situations. The supply of nitrogen from the air is limitless, as well as the content of oxygen. Soviet deposits of water-soluble potassium salts are also enormous, ensuring sufficient amounts for agriculture for millenia. The case of phosphorus is different: the deposits of reasonably rich sources of phosphorites and apatites so far explored can ensure large-scale development of the fertilizer industry for several decades only.

The process of binding nitrogen as synthetic ammonia—used in many countries—is complicated and cumbersome. The electric arc process of binding atmospheric nitrogen and oxygen to form nitric acid and its salts, used at the beginning of the twentieth century in some foreign plant proved uneconomical because of the enormous expenditure of energy and of extremely low efficiency. This problem is being tackled from different directions by various research and pilot-plant establishments in the USSR and abroad. Plasmas, radiolysis, new types of furnaces with high efficiency coefficients, have been studied, as well as the mechanism of the biological utilization of atmospheric nitrogen as its oxides and ammonia in the hope of replicating it technologically. It is to be hoped that all these conjoint efforts will succeed in the next few decades in synthesising economically nitrogen compounds from atmospheric nitrogen.

The research, begun before World War II by the All-Union Institute of Halurgy, into the underground extraction and processing of soluble potassium salts should develop further.

Because of the comparatively limited natural deposits in the USSR of phosphates, geological exploration in Siberia, Central Asia and the Caucasus should be developed; at the same time all possible measures should be taken to work out economic methods of enrichment and chemical processing of low-content, contaminated with undesirable admixtures, phosphorites. The rapid and extensive construction of power stations and the consequently cheaper supplies of energy will result in the more economical electrothermal processing of poor phosphate ores into phosphorus and phosphoric acids. It may become possible to obtain phosphorus anhydride directly through thermal dissociation of calcium phosphates, by-passing the reduction of elementary phosphorus and its oxidation. Similar processes may be of interest in the future in the production of other acid anhydrides.

The contention put forward by Soviet scientists over half a century ago regarding the necessity of developing complex (multiple and mixed) fertilizers including liquid ones, has become universally accepted. Up to the present the widespread use of the considerably cheaper liquid fertilizers has been limited by administrative and technical difficulties, viz. the need to mass-produce machines for introducing them into the soil, to build special storage containers and to ensure transport facilities.

Hydroponics will be developed in northern areas, unsuitable for ordinary agriculture, with conditioned and automated supply of liquid complex fertilizers to the plants.

Chemical industry faces the great and acute problem of satisfying, in the shortest possible time, the qualitative and quantitative needs of animal husbandry for feed-stuffs, preservatives and sanitary agents. Chemical industry has entered the sphere of animal husbandry later than that of horticulture. The economic effect of using feed-stuffs is considerably greater than that of using mineral fertilizers. We shall not dwell here on the numerous problems facing the chemical, petrochemical, silicate and other branches of industry covered by the plans for the immediate future, as these are dealt with in other publications[45].

In view of the rapidly expanding use of pesticides there will be considerable expansion of investigations by chemists, biologists, agriculturists, doctors, veterinary surgeons and other experts to ensure the safety of applying these agents; at the same time steps will be taken to enlighten the users of the agricultural agents. In recent times research organisations and ministries have worked out measures to expand biological and agro-technical means of protecting plants, and to integrate their use with that of chemical agents which are the most quick-acting and most widely-available.

Future researches of chemists and biologist will undoubtedly succeed in combatting various human and animal infectious diseases, malignant tumours, sclerosis, mental and other serious illnesses. Collaboration between chemical and medical establishments and between relevant learned societies could prove very effective in these researches.

FUNDAMENTAL PROBLEMS OF THE SOCIETY

The significance of the activities of learned societies is constantly increasing in view of the rapidly growing rôle of science in industrial progress, penetrating as it does all spheres of life, and in view of the collaboration among various specialists. Naturally, under conditions of socialism and at the time of a scientific-industrial revolution when on the one hand there is growing specialization and division of labour and on the other hand cooperation and integration of effort, the content, form and effect of the work of the Chemical Society must be given special attention and must be perfected. The significance of the resolution of the Soviet Peoples' Committee signed in 1921 by Lenin has not decreased but grown, viz. "...the creation of scientific and technical societies is to be encouraged"[43]. In this document it was submitted that "....engineering and technical societies, in the interests of optimal development and elucidation of technical and economic and administrative problems, (are) to be given all facilities for holding meetings and conferences, for publishing their reports and results of work, and for liason with scientific and technical organizations abroad".

Other government and party resolutions have been of great significance in promoting the effectiveness of scientific and technical societies, especially the resolution of the Council of Ministers of the USSR of 17th October, 1962: "On improvements of the utilization in the national economy of the recommendations of scientific and technical societies".

The Chemical Society has gone a long and honourable way in the last hundred years. The number of members has grown in the past ten years over 50-fold; the activities of the Society have become more diversified and concerned closer with problems posed by life; it takes an active and creative part in socialist construction.

It should be remembered that the Mendeleev Society had initiated the publication of several journals: "Khimiya v Shkole" (Chemistry in the School), "Uspekhi Khimii", Referativnyi Khimicheskii Zhurnal (Journal of Chemical Abstracts), of the popular scientific journal "Khimiya i thizn" (Chemistry and Life), the Journal of the All-Union D. I. Mendeleev Chemical Society, every issue of which publishes a diversified account of a given branch of the science and of technology, its state and problems, thus acting as a live, constantly expanding encyclopaedia of chemistry and

its relationship with the disciplines bordering on it. After the October Revolution the Journal of the Russian Physico-chemical Society split into the Journal of General Chemistry (Zhurnal Obshchei Khimii) and the Journal of Applied Chemistry (Zhurnal Prikladnoi Khimii). In 1920, on the initiative of chemists, was created the Chemico-technological publishing house (now the publishers "Khimiya"[44]).

The annual competitions organized by the Society for the best research work in a given subject attract several thousand scientists each year. A great stimulus is also provided by the annual review of the adoption of new techniques in industry and in institutes; this review is undertaken jointly by the Society and by the trade unions of the petroleum processing industry and of chemical industry and by the ministries concerned.

On the initiative of the All-Union Chemical Society the Government inaugurated in 1965 the award of a Mendeleev Gold Medal for outstanding chemical work of significance to the national economy. The award is made jointly by the Praesidium of the All-Union Chemical Society and the Academy of Sciences of the USSR.

Apart from Mendeleev congresses and numerous conferences and symposia, the Society organizes seminars and schools dealing with chemical achievements and experience; conjointly with the society "Knowledge" lectures and publications are used to disseminate chemical information. Consultations and expert advice services are expanding—especially to industry, to novel undertakings, to workers and young people, to inventors and innovators. A great deal of attention is devoted to everyday problems in chemistry and to local industries.

The most important problem facing the Society in the immediate future is the improvement of the quality of its activities: effectiveness, creative initiative, the involvement in scientific and industrial work of all its members. In the course of recent congresses and plenary sessions of the Society its members were exhorted to take all possible measures to develop independent creative work in divers chemical spheres and to strengthen the contacts and expand the cooperation with physicists, biologists, technologists and other specialists. At the present time the Mendeleev Society is endeavouring to enhance the interest in, and the quality of, theoretical and research studies, attracting a wider circle of young scientists and especially of students.

The current economic reforms necessitate further efforts by economists and engineers to perfect the planning and stimulation of industry, the prognosis of the directions in which chemistry will benefit the national economy, the optimal geographical placing of industrial plant, the methodology of technical economic estimates in industry and in science.

It must be noted with great satisfaction that many retired chemists continue with extremely useful activities, viz. as consultants, experts, organizers; giving guidance to young scientists working for higher qualifications and solving scientific and technical problems.

The complexity of many problems to be solved demands increasingly efficient organization, and the selection and education of gifted, erudite, highly educated organizers and leaders with a great deal of initiative; their numbers are still deficient in the USSR.

Problems arising from the progress of science and technology necessitate continuing searches along the limitless routes of chemical synthesis and continuing expansion of the assortment and properties of the countless products; the physico-chemical mechanisms of chemical reactions have to be studied in depth; technological processes have to be intensified and improved; methods and agents for harmless and safe chemical industrial processes have to be developed, and nature and people have to be safeguarded; research has to be speeded up and the tempo of assimilation of novel techniques by industry has to be accelerated.

This acceleration and a decrease in the cost of experimental work is aided by the efforts of members of the Society who are intensifying the study and application of powerful new means, viz. mathematics, computer techniques, automation and cybernetics, of pilot-plant work and of developing optimal conditions for chemical processes.

The Society has to respond to the pulse of life, to recognize as quickly as possible "growing points" and to ensure their development.

Chemical propaganda at the present time is carried on on a higher plane: it reaches deeper and is directed not only to dissemination of basic information to a wide public but aims at the raising of qualifications of chemists who are specialists in borderline topics of chemistry and technology. The spasmodic lectures and discussions, on the most popular level, are increasingly giving way to systematic cycles of lectures, schools, seminars, laboratory sessions and excursions. Because of the wide range and many-sidedness of the Society's activities the Praesidium is entertaining hopes of creating "Houses of Chemistry".

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Modern chemistry in a socialist state is a powerful and noble force, increasing productivity and helping to raise the level of well-being and culture of the people.

In celebrating the centenary of the "chemical troop" we are not only surveying with legitimate pride the Society's record of successes whilst analysing the mistakes and shortcomings, but we also look to the future, and hope to inspire and direct our members to new creative efforts "for the common harvest", to accelerate the achievement of a happy, thriving human society.

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Halogen Derivatives of Alkyl(or aryl)halogenosilanes and Tetrasubstituted Silanes

K.A.Andrianov and A.I.Petrashko

In recent years there have been many investigations in the field of organosilicon compounds containing halogen-substituted organic groups. These investigations offer prospects of the use of these compounds in the synthesis of polyorganosiloxanes. The extensive data on methods of synthesis of halogen derivatives of alkyl(or aryl)halogenosilanes and tetrasubstituted silanes, their properties, and use are scattered in many periodicals. Monographs and review articles have so far examined only isolated aspects of the chemistry of organosilicon compounds[1-4]. This has stimulated us to survey the accumulated experimental results, the analysis of which even now allows definite regularities to be found in the occurrence of certain reactions and processes in the synthesis and conversions of halogen derivatives of organosilicon compounds. There is a bibliography of 677 references.

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I. METHODS OF SYNTHESIS

1. Halogenation of Alkyl(or aryl)halogenosilanes and Tetrasubstituted Silanes

When halogens act on organosilicon compounds two reactions are possible: (1) detachment of an alkyl or aryl group from a silicon atom, for example, in the bromination of tetraphenylsilane[5,6]:

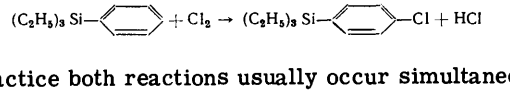
$$(C_6H_5)_4Si + Br_2 \rightarrow (C_6H_5)_3SiBr + C_6H_5Br,$$

or in the halogenation of a trialkylhalogenosilane[7]:

$$R_3SiX + X'_2 \rightarrow R_2SiXX' + RX',$$

where R = alkyl, and X and X' are halogens.

Depending on the halogen attached to the silicon in the alkylhalogenosilane(X), the rate of this reaction increases in the order Br < Cl < F < I. (2) Halogenation of the alkyl and aryl groups of the organosilicon compound, for example, in the chlorination of triethylphenylsilane[8]:



In practice both reactions usually occur simultaneously. The predominating direction of the reaction depends on the conditions under which the process is carried out, and also the catalyst type.

a. Halogenation of alkylhalogenosilanes and tetra-alkylsilanes. The first studies of the chlorination of alkylchlorosilanes and tetrasubstituted alkylsilanes date back to 1945[9].

The chlorination of alkylchlorosilanes and tetra-alkylsilanes can be brought about by the action of chlorine in the liquid or the gaseous phase or by the action of sulphuryl chloride. The photochemical chlorination of methylchlorosilanes, depending on their structure, takes place at different rates, and leads to the formation of chloro(chloromethyl)silanes with different degrees of substitution[10-12].

In liquid-phase chlorination of chlorotrimethylsilane in the presence of azobisisobutyronitrile the composition of the reaction products depends mainly on the ratio of $(CH_3)_3SiCl$ to Cl_2. With increase in this ratio the proportion of polychloro-substituted derivatives diminishes and the yield of $CH_2ClSi(CH_3)_2Cl$ increases[13]. When $(CH_3)_3SiCl : Cl_2 = 1 : 4.15$ the chlorination proceeds with the formation of appreciable quantities of $CH_3.SiCl.(CH_2Cl)_2$ [14] and also of tri- and tetra-substituted derivatives[15]. Further chlorination in CCl_4 leads to the formation of chlorotris(trichloromethyl)silane in 50% yield.

Dichlorodimethylsilane and trichloro(methyl)silane are chlorinated with greater difficulty than chlorotrimethylsilane. It was found[14-19] that the replacement of one methyl radical in chlorotrimethylsilane by a chlorine atom reduces the rate of chlorination by a factor of nine. Unlike chlorotrimethylsilane, in the chlorination of dichlorodimethylsilane by chlorine the hydrogen atoms of a single methyl group are replaced successively[14,16]. Increasing the reaction temperature from 0° to 24.4°C increases the rate of the process three times, but the ratio between the rates of chlorination of $CH_2ClSiCl_3$ and CH_3SiCl_3 is retained. In chlorination by gaseous chlorine at 60°C in the presence of azobisisobutyronitrile, dichlorobis(trichloromethyl)silane is formed in 40–50% yield[17]. The reaction is accompanied by the formation of CCl_4 and CCl_3SiCl_3 as side-products[18]. The chlorination of $CH_3(CCl_3)SiCl_2$ under analogous conditions leads to the formation of $(CCl_3)_2SiCl_2$ in ~ 60% yield. In the liquid-phase photochemical chlorination of trichloro(methyl)silane CCl_3SiCl_3 is formed predominantly[20-23].

The considerable difference in the rates of chlorination of the methyl and chloromethyl groups connected with a silicon atom hinders the production of trichloro(chloromethyl)silane, which is usually obtained by carrying out the reaction with a great excess of trichloro(methyl)silane[24] or by continuously removing the trichloro(chloromethyl)-silane from the reaction zone[25-33]. The chlorination by this method of trichloro(methyl)silane, dichlorodimethylsilane, chlorotrimethylsilane, and tetramethylsilane gives the corresponding monochloro-derivatives in good yields[16,28,34,35].

The use of azobisisobutyronitrile as initiator in the chlorination of chlorotrimethylsilane, unlike the initiation by ultraviolet light, allows $CH_2ClSiCl_3$ to be obtained even in conditions which do not provide for the removal of the chlorination product from the reaction zone[36], which shows

that the nature of the initiator has a significant effect on the chlorination.

In the liquid-phase chlorination of trichloro(methyl)silane and of dichlorodimethylsilane, acetylcyclohexylsulphonyl peroxide is a better initiator for the process than azobisisobutyronitrile[37] but the use of the former helps to increase the yield of polychloro-derivatives.

Tetramethylsilane is readily chlorinated in liquid-phase chlorination[38], just as is neopentane[7]. Here, as for chlorotrimethylsilane, the introduction of a second chlorine atom into the molecule leads to the formation of $(CH_3)_2Si(CH_2Cl)_2$.[39] In the photochemical chlorination of trichloro(methoxy)silane[40,41], a mixture of $CH_2ClOSiCl_3$ and CCl_3OSiCl_3 is formed[42].

With fluorine as the initiator, the chlorination of chloro(methyl)silanes takes place in the dark[43,44]. $CH_2Cl.SiCl_2.CH_3$ was obtained in 50.2% yield from dichlorodimethylsilane by this method, and $(CH_3)_2SiCl.CH_2Cl$ (40.9%) and $(CH_3)_2SiCl.CHCl_2$ (3.8%) from the chlorination of chlorotrimethylsilane. The chlorination of trichloro(methyl)silane under the action of γ-radiation takes place at a high rate[45,46]. The chlorination of poly(dimethylsiloxane) rubber at 0°C under the action of γ-radiation (^{60}Co source) proceeds readily up to the introduction of an average of two chlorine atoms in the polymer unit, after which the rate of the process drops sharply[47]. The chlorination of poly(dimethylsiloxane) rubber by elemental chlorine in CCl_4 in the presence of azobisisobutyronitrile is slow and accompanied by decomposition with formation of difficultly soluble polymers[48].

$(CH_3)_3Si.SiCl.(CH_3)_2$ (25%) and $[CH_2Cl(CH_3)_2Si]_2$ (5.0%) are obtained in the chlorination of hexamethyldisilane[49].

Under the action of chlorine, especially on prolonged chlorination, methylsiloxanes decompose with rupture of the siloxane bond[30,50-55], owing to the hydrogen chloride which is formed.

When the reaction is carried out under mild conditions and the chlorination products are removed continuously from the sphere of the reaction, breaking of the Si–O–Si bonds can be avoided. For example, in the chlorination of octamethylcyclotetrasiloxane[30,56-58] chloromethylheptamethylcyclotetrasiloxane is obtained; more extensive chlorination in the presence of azobisisobutyronitrile leads to the formation of a difficultly separable mixture of chloro-substituted derivatives[59].

On initiation with ultraviolet light tetraethylsilane is chlorinated with the formation of monochloro- and dichloro-derivatives; the reaction is accelerated by phosphorus(V) chloride[60-62].

The photochemical chlorination of chloro(ethyl)silanes with removal of the chlorination products from the reaction zone allows the trichloro-(1-chloroethyl)- and trichloro-(2)-chloroethyl)-silanes to be obtained in 1 : 1.6 ratio[63-68]. The vapour-phase chlorination of trichloro(ethyl)silane at 350°C leads to the formation of 1- and 2-chloroethyl derivatives[69] in the ratio 1 : 1.08. In the chlorination of dichloro(ethyl)methylsilane under ultraviolet irradiation dichloro(chloromethyl)ethylsilane is formed predominantly[70]. When the reaction is carried out with illumination from a 150 W electric lamp (16–21°C) dichloro-(1-chloroethyl) methylsilane can be obtained in 38% yield on the dichloro(ethyl)methylsilane which has reacted. $CF_2HCF_2SiCl_3$ is chlorinated at 150–200°C with the formation of $CF_2ClCF_2SiCl_3$.[71]

The chlorination of trichloro(propyl)silane leads to the formation of α-, β-, and γ-chloro-derivatives in the ratio 0.7 : 1 : 1.[31] Trichloro-(isopropyl)silane is chlorinated with preferential formation of trichloro-(2-chloro-1-methylethyl)silane[72]. A necessary condition for obtaining the monochloro-derivatives in the chlorination of the trichloro-(propyl)silanes is the removal of the chlorination products from the reaction zone[73-76].

In the chlorination of $CF_3CH_2CH_2SiCl_3$ under the action of ultraviolet radiation[77] the C–H bond in the α-position is 6.2 times more susceptible to attack by chlorine than that in β-position. At the ratio $Cl_2 : CF_3CH_2CH_2SiCl_3 = 1.5$ and 25–100°C, 80% $CF_3CH_2CHClSiCl_3$ and 20% $CF_3CHClCH_2SiCl_3$; $CF_3CH_2CCl_2SiCl_3$ is formed as an impurity. The predominant formation of the α-chloro-derivatives also occurs in the chlorination of $CF_3CH_2CH_2Si(CH_3)Cl_2$.[78] Consequently the CF_3 group acts more strongly than the dichloro(methyl)-silyl and trichlorosilyl groups as β-orienting agents.

Trichloro(vinyl)silane is chlorinated differently depending on the temperature: at 200–350°C substitution occurs with the formation of $CH_2=CClSiCl_3$; at 160–200°C chlorine adds at the double bond with the formation of $CH_2ClCHClSiCl_3$.[79] Trichloro(methylallyl)silane is chlorinated with replacement of hydrogen in the methyl group even at room temperature[80,81]:

$$Cl_3SiCH_2C(CH_3)=CH_2 \xrightarrow{Cl_2} Cl_3SiCH_2C(CH_2Cl)=CH_2 .$$

Substitutional chlorination also takes place with trichloro(isocrotyl)silane[82]; however, the addition of chlorine in the chlorination of alkenyl- and (alkenyl)alkylchlorosilanes is the main reaction[21,23,74,79,83-86].

A series of studies was devoted to the chlorination of hexachlorodisilylmethane[31,37], hexachlorodisilylethane[31,88], and other compounds of this type[39,89,90]. In the photochlorination of 1,1,3,3,5,5,7,7-octachloro-1,3,5,7-tetrasilacyclo-octane[91] 1,1,2,2,3,3,4,5,5,6,7,7,8-tridecachloro-1,3,5,7-tetrasilacyclo-octane is formed.

Chlorocyanoalkyl-substituted silanes of the general formula

$$[NC(CH_{2-a}Cl_a)_b]_n SiR_mX_{4-m-n}$$

where $a = 1$ or 2, $b = 2$–12, $n = 1$–3, $m = 0$–2, and X = Cl or F, are obtained by chlorination with elemental chlorine at 20–80°C and ultraviolet irradiation of the corresponding cyanoalkyl-substituted halogenosilanes[92].

Chlorination of alkylchlorosilanes and alkyl-substituted esters of orthosilicic acid by sulphuryl chloride takes place on heating in the presence of benzoyl peroxide[93-95].

Sulphuryl chloride is a less active chlorinating agent, therefore it is recommended for the chlorination of chloro(methyl)silanes when the formation of polychloro-derivatives must be avoided[96].

In the chlorination by sulphuryl chloride of chlorotrimethylsilane in the presence of peroxide in chlorobenzene as medium chloro(chloromethyl)dimethylsilane is formed[97,98]. Trichloro(methyl)silane in a medium of *o*-dichlorobenzene at 80°C is chlorinated by sulphuryl chloride to trichloro-(chloromethyl)silane, but its yield is only ~ 2.6%[23].

Under ultraviolet irradiation dichlorodimethylsilane reacts with sulphuryl chloride with great difficulty, giving a small quantity of dichloro(chloromethyl)methylsilane[99].

Owing to their higher boiling points chloro(ethyl)silanes are readily chlorinated by sulphuryl chloride in the absence of solvents; 1- and 2-chloroethylchlorosilanes are formed as a result[21,93,100]. The ethyl group is chlorinated more easily than the methyl group. Thus in the chlorination by sulphuryl chloride of dichloro(ethyl)methyl silane the main products are dichloro-(1-chloroethyl)methylsilane and dichloro-(2-chloroethyl)methylsilane[101]. Tetraethylsilane forms 1-chloroethyl derivatives[28,63,102,103]; in the chlorination of trichloro(ethyl)silane, dichlorodiethylsilane, and

chlorotriethylsilane, mixtures of chloro-(1- and 2-chloroethyl)silanes are formed [93,100,104]. The yield of the 2-isomers increases with the increase in the number of chlorine atoms at the silicon [64].

Chlorination of trichloro(propyl)silane by sulphuryl chloride leads to the formation of the 1-, 2-, and 3-isomers [108] in the ratio 1 : 3.5 : 3.1; trichloro(isopropyl)silanes give a mixture of the 1- and 2- isomers [106] in the ratio 1 : 3.5. Trichloro-(t-butyl)silane forms $CH_2Cl(CH_3)_2C.SiCl_3$ on chlorination [107]. Hexamethyldisilane is chlorinated by sulphuryl chloride to chloromethylpentamethyldisilane [108].

Organosilicon alcohols, can be easily converted into the corresponding halogen derivatives with hydrogen halides [109-111,113], thionyl chloride [112-115], phosphorus(III) bromide [116-119], etc.

Sulphuryl chloride readily chlorinates bis(trichlorosilyl)-methane and bistrichlorosilylethane [31] and also cyclocarbosilanes containing chlorine atoms [120,121] and methyl groups [122] at the silicon.

t-Butyl hypochlorite is also used as a chlorinating agent in the chlorination of alkyl-substituted organosilicon compounds [123,124].

Tetrasubstituted silanes are brominated directly by bromine [125-127] and by bromosuccinimide [128-130]. In the bromination of tetraethylsilane $(C_2H_5)_3SiCHBrCH_3$ and $(C_2H_5)_3SiCBr_2CH_3$ [25,28-33] are formed [134]. Chloro(methyl)-silanes and tetramethylsilanes have been brominated by ultraviolet irradiation and the simultaneous passage of bromine and chlorine [135]. Bromination of chloro(ethyl)silanes in this way gives a mixture of 1- and 2-bromoethylsilanes [136,137]. Under these conditions hexamethyldisiloxane forms bromomethylpentamethyldisiloxane [138]. Trichloro-(2-cyanoethyl)silane is brominated with formation of bromocyanoethyltrichlorosilane [139]. The bromination of 1,1,2-triphenyl-1-silacyclobutane with *N*-bromosuccinimide leads to the formation of 2-bromo-1,1,2-triphenyl-1-silacyclobutane [140].

When bromine acts on unsaturated alkenylchlorosilanes and alkenylalkylsilanes addition of bromine at a multiple bond takes place [71,141-143].

b. Halogenation of arylhalogenosilanes, arylalkylhalogenosilanes, and tetra-aryl (or arylalkyl)-substituted silanes. Ladenburg carried out the direct chlorination of triethoxy(phenyl)-silane [144] but an intensive study of this process began in the 1940's after the appearance of a patent [145] on the chlorination of dichlorodiphenylsilane and dichloro(methyl)phenylsilane.

The chlorination of the aromatic nuclei of organosilicon compounds takes place in the presence of catalysts: metallic iron, iodine, phosphorus(V) chloride, antimony(III) chloride, or aluminium chloride, and is initiated by ultraviolet light [146].

There have been many studies of the chlorination of trichloro(phenyl)silane [147-159]; in these investigations the production of trichlorochlorophenylsilanes of all degrees of substitution of chlorine for hydrogen in the phenyl group under various conditions was investigated using radical catalysts.

The chlorination of chloro(phenyl)silanes in the presence of iodine and phosphorus(V) chloride takes place at 110-140°C without splitting of the chlorination products, but the catalytic activity of these substances is low. They can therefore be used for obtaining monochloro-derivatives of trichloro(phenyl)silane and dichlorodiphenylsilane. ICl and ICl_3 react with trichloro(phenyl)silane at low temperature (-40°C) with the formation of $C_6H_5 - nCl_nSiCl_3$ ($n = 1$ or 2), the main reaction product being trichloro-(*m*-chlorophenyl)silane [160]. The reaction of $Cl_2C_6H_3SiCl_3$ with ICl_3 at 20°C leads to $Cl_3C_6H_2SiCl_3$. Photochemical chlorination of trichloro(phenyl)silane in the presence of iodine at 20°C leads to the formation of a product of incompletely additive chlorination [161] $C_6H_5Cl_4SiCl_3$.

The splitting of the Si-C bond in the presence of catalysts increases with the chlorination temperature; it can be reduced to a minimum by carrying out the reaction under milder conditions (for example, at 20-30°C in a medium of carbon tetrachloride or some other solvent which is inert in relation to chlorine). When aluminium chloride or iron(III) chloride is used as catalyst splitting of the reaction products takes place even at 30°C—at the very start of chlorination. In the presence of antimony(III) chloride this process is observed in more extensive chlorination and at higher temperatures [162].

In the chlorination of dichlorodiphenylsilane at 70-80°C in the presence of antimony(V) chloride the process takes place with considerable evolution of heat; the main product of the reaction is dichlorobistrichlorophenylsilane. Dichlorobispentachlorophenylsilane can be obtained by further chlorination at 120°C but then the splitting of the Si-C bond can be considerably intensified.

Chlorination at 100°C and over without catalysts or chlorination with irradiation of the reaction mixture with ultraviolet light at 70°C does not bring about splitting of the Si-C bond in trichloro(phenyl)silane or dichlorodiphenylsilane.

Temperature has a considerable influence on the nature of the chlorination of trichloro(phenyl)silane in light (there is no reaction in the dark) and in ultraviolet radiation [158,161,163]. At 0-2°C addition of chlorine occurs, at 95-100°C as well as the addition there is replacement of hydrogen atoms of the phenyl group by chlorine; at 125-150°C the reaction is more vigorous than in the presence of azobisisobutyronitrile.

Depending on the chlorination conditions, the $SiCl_3$ group exhibits a different orienting effect. In chlorinating trichloro(phenyl)silane in the presence of iron a mixture of *m*-, *p*-, and *o*-chlorophenyltrichlorosilanes in the ratio 74 : 2 : 24 is formed [150], but in the chlorination of trifluoro-(phenyl)silane the ratio is 82 : 0 : 18 [164]. This shows that the trichlorosilyl and trifluorosilyl groups orient the replacement of hydrogen of the benzene nucleus by chlorine, mainly in the *meta*-position. Chlorination of trimethyl-(phenyl)silane gives a mixture of the *o*-, *p*-, and *m*-chlorophenyltrimethylsilanes in the ratio 24 : 25 : 51 [164].

In the electrophilic chlorination of trichloro(phenyl)-silane in the presence of $FeCl_3$ and $AlCl_3$ and $SiCl_3$ group is also a *meta*-orientant; 28% of the *ortho*-isomer is formed [159].

In the photochemical chlorination of trichloro(phenyl)-silane at 120-150°C in the presence of azobisisobutyronitrile 43% *o*-$ClC_6H_4SiCl_3$ is formed. When iodine is used as catalyst (whether with illumination or in the dark) at 20°C 67% trichloro-*o*-chlorophenylsilane and $C_6H_5Cl_4SiCl_3$ is formed.

The polymers which contain phenyl groups at silicon atoms are converted during chlorination into the corresponding polymers with chlorophenyl groups [165].

It should be noted that the distribution of chlorine between the phenyl groups in the fractions is irregular: the degree of chlorination increases with decrease in the molecular weight of the fraction.

The chlorination of *p*-chlorophenyltrichlorosilane, trifluoro(phenyl)silane [164] and tetraphenylsilane [166] is effected

in the presence of $FeCl_3$ and $SbCl_5$ as catalysts in CCl_4 medium to decrease cleavage of the Si–C bond.

When there are alkyl substituents at the phenyl group they are the first to be chlorinated. In the chlorination of trichloro-*p*-tolylsilane, trichloro-*p*-trichloromethylphenylsilane is obtained[167,168]; when the process is carried out with ultraviolet irradiation trichloro-*p*-trichloromethylphenylsilane can be obtained in 92% yield. Trichloro-*o*-tolylsilane under these conditions is not chlorinated, owing to steric hindrance by the $SiCl_3$ group[168], whereas trifluoro-*o*-tolylsilane is chlorinated readily.

The chlorination of trichloro(ethyl)phenylsilanes lead to the production of $C_2H_5 - {}_nCl_nC_6H_4SiCl_3$ [169] and p-$CH_2ClCH_2 . C_6H_5SiCl_3$ [170,171]. Trichloro(*p*-ethylphenyl)silane is readily chlorinated on illumination with two luminescent lamps; the p-$C_2H_4ClC_6H_4SiCl_3$ which is formed is used to obtain p-$CH_2{=}CHC_6H_4SiCl_3$.[170,172–174].

Compounds in which the phenyl groups are connected with silicon by methylene links are readily chlorinated by sulphuryl chloride[175]:

$$C_6H_5CH_2SiCl_3 \xrightarrow{SOCl_2} C_6H_5CH_{2-n}Cl_nSiCl_3.$$

A series of compounds of this type was obtained by this reaction, for example, $C_6H_5CHClSi(CH_3)_3$, and $(C_6H_5)_2 . CClSi(CH_3)_3$ [93,176–178] and also chloro-substituted benzyltrichlorosilane and trichloro-(-*p*-xylenyl)silane[176].

The direction of the chlorination of dichloro(methyl)phenylsilane is determined by the conditions. The use as catalysts of $FeCl_3$ and $SbCl_5$,[180] $SbCl_3$ at 10–15 °C, and also iodine (the reaction being carried out in CCl_4 or without a solvent)[181] leads to substitution of chlorine for hydrogen atoms in the phenyl groups; chlorination of the methyl groups does not take place under these conditions, but the reaction is accompanied by splitting of the $Si-C_{aryl}$ bond, the splitting proceeding more readily than with dichlorodiphenylsilane. The CH_3SiCl_2 group, like the $SiCl_3$ group, orients the replacement of hydrogen in the benzene nucleus by chlorine mainly into the *meta*-position.

In the presence of azobisisobutyronitrile the chlorination of dichloro(methyl)phenylsilane takes place with the chlorine replacing hydrogen atoms in the methyl group; the product of exhaustive chlorination at 110–115 °C is $C_6H_5(CCl_3)SiCl_2$.[182,183]

In the photochemical chlorination of dichloro(methyl)phenylsilane at 20–25 °C in addition to the substitution of chlorine for the hydrogen atoms in the methyl groups[163] addition of chlorine to the phenyl group takes place[184].

The chlorination of dichloro(methyl)phenylsilane in diffuse daylight proceeds in different directions depending on the temperature of the reaction. At 0–5 °C the only reaction is addition of chlorine to the phenyl group with the formation of dichloro(methyl)(hexachlorocyclohexyl)silane in 78.4% yield[185]; raising the temperature of the reaction to 20–25 °C leads to a decrease in the yield of $C_6H_5Cl_6(CH_3) . SiCl_2$ to 46% owing to the formation of dichloro(dichlorophenyl)methylsilane (19.6%)[163,186]. With a further rise in the chlorination temperature the substitution reaction rate increases and at 50–55 °C replacement of hydrogen by chlorine in the phenyl group takes place exclusively[187], with the formation of $C_6H_5 - {}_nCl_n(CH_3)SiCl_2$ (n = 2 or 3); the CH_3SiCl_2 group is a *meta*-orientant here.

Unlike dichloro(methyl)phenylsilane, dichloro(phenyl)(trichloromethyl)silane does not react with chlorine in diffuse daylight at 110–115 °C in the absence of initiating and catalysing additions[188]. On raising the temperature to 150 °C the $Si-C_{aryl}$ bond is broken. In the presence of $SbCl_3$ or iodine, $C_6H_5 - {}_nCl_n(CCl_3)SiCl_2$ is formed (n = 1–3). Like $SiCl_3$, the CCl_3SiCl_2 group directs the chlorine atom entering the phenyl nucleus mainly into the *meta*-position.

$C_6H_4Cl_6(CCl_3)SiCl_2$ is formed in the photochemical chlorination of $C_6H_5(CCl_3)SiCl_2$ at 20–25 °C. Analogous results are given by azobisisobutyronitrile as initiator. The increased stability of $C_6H_5(CCl_3)SiCl_2$ in comparison with $C_6H_5(CH_3)SiCl_2$ in electrophilic and radical chlorinations is explained by the increaee in the electrophilic nature of the silicon atom in $C_6H_5(CCl_3)SiCl_2$ owing to replacement of the electron-donating methyl group by the electron-accepting trichloromethyl group.

In the chlorination of $(p$-$CH_3C_6H_4)CH_3SiCl_2$ in the presence of azobisisobutyronitrile at 110–115 °C by chlorine the hydrogen in the methyl group of the aromatic nucleus is replaced first[189]. Trichloromethyltriphenylsilane is formed in the chlorination of methyltriphenylsilane[190].

The chlorination of dichloro(methyl)phenylsilane with the aid of sulphuryl chloride in the presence of radical catalysts takes place with substitution of chlorine for the hydrogen atoms in the methyl groups[191]; the main product of the reaction when the process is carried out in the presence of azobisisobutyronitrile is $C_6H_5(CHCl_2)SiCl_2$.

The chlorination of dichloro(methyl)phenylsilane under the action of radiation (^{60}Co) leads to the formation of $C_6H_2Cl_3(CCl_3)SiCl_2$.[47] In the chlorination of polyphenylmethylsiloxanes under these conditions, in addition to substitution additive chlorination in the phenyl nucleus also takes place under these conditions[47,192].

The production of bromoarylchlorosilanes by the direct bromination of aryltrichlorosilanes and diaryldichlorosilanes is accompanied by cleavage of the Si–C bond. This reaction is especially prominent in the synthesis of the polybromophenylchlorosilanes.

Bromophenyltrichlorosilane was obtained in 40% yield by the simultaneous action of bromine and chlorine on trichloro(phenyl)silane with irradiation by ultraviolet light[135,193]. The bromination of trifluoro(phenyl)silane in the presence of iron gives pronounced splitting of the Si–C bond; the yield of bromophenyltrifluorosilane is only 3.5%.

Of the other aromatic chlorosilanes there have been studies of the bromination of benzyltrichlorosilane[194], trichloro-(*p*-tolyl)silane[195], and tetra-(*p*-tolyl)silane[196]. It was found that the $-(CH_2)_nSiCl_mR_{3-n-m}$ groups are strong *ortho*- and *para*-orienting agents and activate the benzene ring in electrophilic substitutions[197].

Benzyltrimethylsilane is brominated more readily than benzyltrichlorosilane[198]; on boiling a solution of it in CCl_4 with *N*-bromosuccinimide $C_6H_5CHBrSi(CH_3)_3$ and $C_6H_5CBr_2Si(CH_3)_3$ are formed[177]. In the bromination of $R_3SiCH(C_6H_5)_2$, $R_3SiC(C_6H_5)_2Br$ is obtained in yields up to 96%.[199] p-$CH_2BrC_6H_4Si(C_6H_5)_3$ is obtained by an analogous method[128]. o-$CH_2BrC_6H_4Si(C_6H_5)_2Br$ was obtained by the action of *N*-bromosuccinimide on o-$CH_3C_6H_4Si(C_6H_5)_2H$.[200] *N*-Bromosuccinimide readily brominates 2:3-benz-1-silacycloalkanes[201] to form 4-bromo-substituted derivatives.

The formation of p-bromobenzyltrifluorosilane in the bromination of benzyltrifluorosilane takes place without cleavage of the Si–C bond[164].

The bromination of dichloro(methyl)phenylsilane in the absence of a catalyst at 0°–25 °C leads to the production of $C_6H_5 - {}_nBr_n(CH_3)SiCl_2$ and is not accompanied by Si–C bond cleavage[202]. With catalysts (iodine, $SbCl_3$) at 10–15 °C the formation of these products is accompanied by $Si-C_{aryl}$ bond cleavage. In both instances the CH_3SiCl_2 group is a *meta*-orientant.

In the bromination of $BrC_6H_4Si(CH_3)_3$ 92.5% trimethylbromosilane and 92.7% dibromobenzene are formed.

The bromination of arylsilanes containing acetamido-[203], dimethylamino-[204], and hydroxyl[205] groups in the phenyl

group and of 9-fluorenyltrimethylsilane[206] has also been studied.

2. Addition of a Triorgano(halogeno)silyl Group to Unsaturated Halogenohydrocarbons

The addition of a triorgano(halogeno)silyl group to unsaturated halogenohydrocarbons was first effected at the start of the 1950's[207,208].

The addition of silanes to halogeno-substituted ethylenes takes place with greater difficulty than to ethylene. Depending on the type and number of halogen atoms in the molecule, the halogen-substituted ethylenes can be arranged in the following series of decreasing reactivity in the presence of platinum catalysts[209-213]: $CH_2=CH_2 > CH_2=CF_2 > CF_2=CFCl > CF_2=CF_2$.

Dichloro(alkyl)silanes add with difficulty to tetrafluoroethylene in the presence of platinum or palladium on carriers[211,214,215], $H_2PtCl_6.6H_2O$,[211,213] and under the action of γ-radiation[216]. Better results are obtained on initiation with ozone[217-219]; the maximal yield of addition products occurs on initiation of the reaction with ultraviolet light[220-223]. Under these conditions SiH_4 adds to $CF_2=CF_2$ with the formation of tetrafluoroethylsilanes of all degrees of substitution[224].

Trichlorosilane adds more readily to halogenoethylenes, the initiation of the reaction with ultraviolet light also being most effective[225,226].

Radiochemical synthesis with γ-radiation can be effected only when the rate of polymerisation of the halogenoalkene is lower than that for the addition. The maximal yield of addition products occurs when the initial mixture of reagents contains 1 mole alkene per hydrogen atom of silane[216].

Alkenes of the general formula $RR'C=CR''R'''$ add silanes of the formula $SiH_{4-m-n}X_nZ_m$ (where X is halogen, Z alkyl, $n = 2$ or 3, $m = 0$ or 1, and R, R', R'', and R''' are H, alkyl or aryl, at least one group being electronegative) in the presence of catalytic amounts of tertiary amines[227]. The reaction takes place at 25–130°C and pressures of 3.5–17.5 atm.

The order of addition depends on the nature of the compounds reacting and the type of catalyst. In the presence of platinum catalysts silanes add to 1,1-difluoroethylene in such a way that the silyl group will be at the carbon atom of the methyl group:

$$CF_2=CH_2 + HSi\lessgtr \rightarrow CF_2H-CH_2Si\lessgtr .$$

The addition of trichlorosilane to chloroethylene in the presence of benzoyl peroxide proceeds in two directions[224]:

$$CH_2=CHCl + HSiCl_3 \xrightarrow{(C_6H_5COO)_2} \begin{cases} \rightarrow ClCH_2CH_2SiCl_3 \\ \rightarrow CH_3CHClSiCl_3. \end{cases}$$

The order of addition of trichlorosilane to chlorotrifluoroethylene has not been established: some investigators[214,215,228] think that the silyl group adds to the CFCl group; others[225,226], to the CF_2 group.

Silanes react more difficultly with perfluoropropene than with perfluoroethylene[226]. When the double bond is not screened by fluorine atoms the addition proceeds much more readily, although with somewhat greater difficulty than with propene. For example, silanes add to trifluoropropene under the influence of ultraviolet radiation[226,229-231], peroxides[226], platinum on carbon[228,232,233], and $H_2PtCl_6.6H_2O$.[234-236].

In the presence of hydrogen hexachloroplatinate(IV) $HSiCl_3$ adds to $(CF_3)_2C=CH_2$:[237]

$$(CF_3)_2C=CH_2 + HSiCl_3 \rightarrow (CF_3)_2CHCH_2SiCl_3.$$

In the presence of radical initiators dichlorosilane adds to fluorinated alkenes with the formation of compounds of the general formula:

$$(RCF_2CHR'CH_2)_2SiCl_2,$$

where R = H, F or a perfluoroalkyl group, R' = H, CH_3, CF_3, C_2H_5, or C_3F_7.[238]

Difluoropropene $CHF_2CH=CH_2$ adds to organohydrochlorosilanes more readily than $CF_3CH=CH_2$.[239]

$CF_3CF_2CH=CH_2$ [230,240-242] and $CF_3CF_2CF_2CH=CH_2$ [228,229,232,240] react readily with silanes; $CF_3CF_2CF=CH_2$ [226] reacts with greater difficulty. In the presence of hydrogen hexachloroplatinate(IV) compounds of the formulae $HSiCl_3$, $RSiHCl_2$, and R_3SiH add to 3,4-dichlorobut-1-ene exclusively according to Farmer's rule; addition to 1,4-dichlorobut-2-ene is accompanied by the formation of anomalous reaction products[243].

The addition of silanes to allyl chloride proceeds readily under the action of ultraviolet light and peroxides[244], platinum on carriers[245], and complexes of $PtCl_2$.[246] As well as the additions, reduction of the allyl chloride by the silane occurs[247]:

$$CH_2=CHCH_2Cl + HSi\lessgtr \rightarrow \gtrless SiCl + CH_3=CHCH_3.$$

Dichloro(methyl)silane reacts with allyl bromide in the presence of hydrogen hexachloroplatinate(VI) to form $BrCH_2CH_2CH_2Si(CH_3)Cl_2$;[248,249] the reaction is more difficult than that with allyl chloride.

The addition of silanes to methylallylchloride in the presence of platinum on carriers[214,250,251] or $H_2PtCl_6.6H_2O$ [248-252] proceeds with higher yields than for allyl chloride.

The removal of electronegative groups or atoms from the double bond favours an increase in the reactivity of halogenoalkenes in additions[214].

Trichlorosilane adds to *m*- and *p*-$ClC_6H_4CH_2CH_2CH=CH_2$ with the formation of $ClC_6H_4[CH_2]_4SiCl_3$ with $ClC_6H_4CH.(SiCl_3)[CH_2]_3CH_3$ as impurity; the *o*-chloro-substituted addition of trichlorosilane with the formation of only $ClC_6H_4[CH_2]_4SiCl_3$.[253]

The addition of trichlorosilane and dichloro(methyl)-silane to the chlorobutenes in the presence of platinum is accompanied by allyl rearrangement, loss of chlorine in the allyl position, and migration of a double bond[254].

Compounds with a triple bond react with silanes to form alkenylhalogenosilanes. Trichloro-(1,2-dichlorovinyl)silane was obtained in this way[255,256]:

$$ClC \equiv CCl + HSiCl_3 \rightarrow CHCl = CClSiCl_3.$$

This reaction is accelerated in the presence of peroxides, on irradiation with ultraviolet light, or on heating to a temperature close to the decomposition temperature of dichloroacetylene.

In the presence of $H_2PtCl_6.6H_2O$, $RSiHCl_2$ (R = Cl or CH_3) adds vigorously to $CH_2ClC\equiv CH$ with the formation of various amounts of $RCl_2SiCH=CHCH_2Cl$ and $RCl_2SiC(=CH_2)CH_2.Cl$.[257] The reaction with $HC\equiv CCH_2Br$ takes place in a similar manner[258]. 1,4-Dichlorobutyne reacts with $HSiR_xCl_{3-x}$ according to the scheme[243]:

$$CH_2ClC\equiv CCH_2Cl + HSi\lessgtr \rightarrow \gtrless SiC(CH_2Cl)=CHCH_2Cl.$$

Triorganosilanes add to $CX_3CH(OH)OC(CH_3)(CR_2)C{\equiv}CH$ according to the Farmer rule with the formation of

$$CX_3CH(OH)OC(CH_3)(CR_2)CH{=}CHSiR'_3,$$

where R = H or CH_3, X = Cl or Br, R = CH_3, C_2H_5, or C_3H_7.[259]

In reaction with 1,1,2,2-tetrafluoroethylallyl ether[210, 212, 260-262] in the presence of platinum catalysts the alkylhalogenosilanes can be arranged in order of decreasing activity:

$$R_3SiH > R_2SiHCl > RSiHCl_2 > HSiCl_3.$$

Aryldichlorosilanes add most easily to this ether[263].

The addition of R_nSiHX_{3-n} (R = CH_3, C_2H_5; $n \neq 0, 1, 3$; X = halogen) to vinyl ethers of the $R'OCH{=}CH_2$ type (R' = p-ClC_6H_4, 2,4-$Cl_2C_6H_3$), leading to the formation of $R'OCH_2CH_2SiR_nX_{3-n}$, which is accompanied by β-decomposition, which leads to the production of $R'OSiR_nX_{3-n}$.[264]

The direction of the addition of silanes to unsaturated halogenohydrins depends on the position of the double bond relative to the halogen-bound carbon atom[265,266].

In the presence of hydrogen hexachloroplatinate(IV), $HSiCl_3$, CH_3SiHCl_2, and $HSi(OC_2H_5)_3$ adds to 2-chloromethylbicyclo[2,2,1]hept-5-ene,[267]

3. Addition of Halogens to Multiple Bonds of Alkenylsilanes

The addition of halogens proceeds readily to almost any organosilicon compound containing a multiple bond. When the organosilicon compound has at the silicon atom a vinyl group or another group with a double bond in the α-position, then $\alpha\beta$-alkyldihalogenosilanes are formed, which are rather stable thermally:

$$R_3SiCH{=}CH_2 + X_2 \rightarrow R_3SiCHXCH_2X,$$

where X = halogen. When the double bond is in the β-position to the silicon atom then $\beta\gamma$-dihalogenoalkylsilanes are formed in the reaction with the halogens; these are thermally unstable and undergo the so-called β-decomposition[268]:

$$R_3SiCH_2CH{=}CH_2 + X_2 \rightarrow R_3SiCH_2CHXCH_2X \rightarrow R_3SiX + CH_2XCH{=}CH_2.$$

$\beta\beta$-Difluoroalkyl-substituted organosilicon compounds readily decompose at low temperatures, as do $\alpha\alpha\beta\beta$-tetrafluoroethyl-substituted compounds[269]. Compounds with γ- and more distant positions of the double bond relative to the silicon atom readily add on halogens to form stable dihalogenoalkylsilanes. For example, the pyrolysis of trifluoropropyl-substituted organosilicon compounds is observed only at temperatures above 550°C.[269] The thermal stability of the dihalogenoalkylsilanes depends considerably on the nature of the remaining substituents at the silicon atom. The presence of a trichlorosilyl group sharply increases the thermal stability of even $\beta\gamma$-dichloroalkylsilanes.

There have been many studies of the addition of halogens to various alkenosilanes[81,143,268,270-279]. These papers describe the synthesis and properties of a large number of halogenoalkylsilanes. There have been several recent studies of this problem[280-282]. It was found that the replacement of three hydrogen atoms by fluorine considerably decreases the activity of a double bond in the addition of halogens, hydrogen halides, and polyhalogenomethanes[280].

Organosilicon compounds containing silacycloalkenic structures readily add halogens. For example, 1,1-dichlorosilacyclopent-2-ene adds bromine in CCl_4 at 0°C with the formation of 1,1-dichloro-2,3-dibromosilacyclopentene[283]. The reaction of 1,1,3,3-tetramethyl-1,3-disilacyclopentene with bromine and chlorine takes place analogously[284].

In a gas chromatographic investigation of the pyrolysis products of $Si(CH_3)_4$, $(CH_3)_2Si{=}CHSi(CH_3)_3$ was isolated, which vigorously reacts with bromine[285]:

$$(CH_3)_3Si{=}CHSi(CH_3)_3 + Br_2 \rightarrow (CH_3)_3BrSiCHBrSi(CH_3)_3.$$

$(CH_3)_3SiCH{=}C{=}O$, which is formed in the thermal (120-130°C) decomposition of $(CH_3)_3SiC{=}COC_2H_5$, adds on bromine with the formation of $(CH_3)_3SiCHBrCOBr$.[286]

The reaction of 1,1-bis(trimethylsilyl)ethylene with chlorine and bromine leads to the loss of one trimethylsilyl group[287]:

$$[(CH_3)_3Si]_2C{=}CH_2 + X_2 \rightarrow (CH_3)_3SiX + (CH_3)_3SiCX{=}CH_2.$$

The addition of bromine to silyl-substituted acetylenes leads to the formation of vinyl derivatives[141,288-290].

Hydrogen halides add to alkenylsilanes less vigorously than halogens. The presence of chlorine atoms at the silicon atom strongly retards and the presence of three alkyl groups accelerates the addition of hydrogen halides. On transferring the multiple bond from the α and β position the rate of addition increases, but further in the γ position, it falls. The rate of addition of hydrogen halides to alkenylsilanes increases in the order: HCl < HBr < HI. The addition of hydrogen halides, with the exception of hydrogen bromide, to allyl- and methylallyl-alkylsilanes takes place according to Markovnikov's rule independently of the nature of the alkyl groups connected to the silicon[291-295].

The reaction of vinyl-containing organosilicon compounds with hydrogen halides was first effected by the scheme[296]:

$$(CH_3)_3SiCH{=}CH_2 + HI \rightarrow (CH_3)_3SiCH_2CH_2I.$$

Subsequent investigations[275,292,297-300] showed that the addition of hydrogen halides to vinylsilanes takes place contrary to the Markovnikov rule. Just as for halogens, $CF_2{=}CFSi(C_2H_5)_3$ adds hydrogen halides worse then $CH_2{=}CHSi(C_2H_5)_3$.[280] HBr can add to $(CH_3)_3SiCH_2CH_2CH{=}CH_2$ both according to and contrary to the Markovnikov rule[116,204].

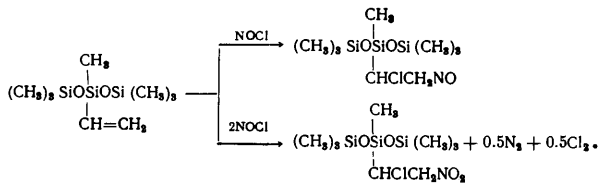
The addition of HBr and HCl to isopropenyltrimethylsilane[82,275,301] and isocrotyltrimethylsilane[82,300,302] obeys the Markovnikov rule, whereas HBr adds to $\alpha\beta$-dimethylvinyltrimethylsilane and $\gamma\gamma$-dimethylallyltrimethylsilane contrary to the Markovnikov rule[82].

Hydrogen halides add to silacyclopentenes with the formation of the corresponding halogeno-substituted silacyclopentanes[283,284].

As already noted, the β-halogenosilanes formed on addition of hydrogen halides to $\alpha\beta$-unsaturated silanes are extremely unstable compounds, which readily undergo β-decomposition with various reagents[173,303] or on raising the temperature[304-306]. The kinetics of the thermal decomposition of trichloro-2-chloroethylsilane[305] and 2,2-difluoroethyltrifluorosilane[307] in the gas phase follow a first-order equation.

Depending on the type of trimethylsilylalka-1,5-diyne, the addition to it of halogens and hydrogen halides proceeds differently[308]: (a) bromine adds to trimethylsilyldipropargyl at both triple bonds; (b) it adds to 1-trimethylsilylocta-1,5-diyne predominantly at the triple bond unsubstituted by silicon. HBr adds to 1-trimethylsilylhexa-1,5-diyne at the disubstituted triple bond with partial splitting of the adduct along the C–Si bond.

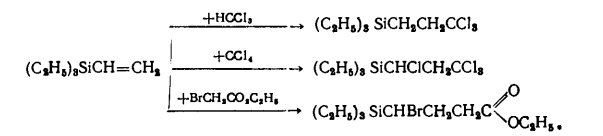
The nitrosochlorination of the vinyl-containing organosilicon compounds takes place in two directions[309]:



$ClNO_3$ adds to vinyltrichlorosilane according to the reaction[310]:

$$Cl_3SiCH{=}CH_2 + ClNO_3 \rightarrow Cl_3SiCHClCH_2NO_3.$$

The addition of polyhalogenomethanes and other halogenated hydrocarbons to vinylsilanes takes place with high yields, according to the reactions[280,311-316]:

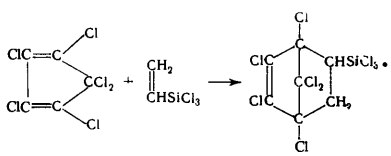


Polyhalogenohydrocarbons containing fluorine also add to vinyl-containing compounds[313,314,316,318].

When $CHCl_3$ and t-C_4H_9OK react with vinyl- and allyl-containing organosilicon compounds, products with dichlorocyclopropane groups are formed[319-322]:

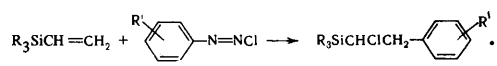
$$\equiv Si[CH_2]_nCH{=}CH_2 + CCl_2 \rightarrow \equiv Si[CH_2]_n\overline{CHCH_2CCl_2}.$$

Trichloro(vinyl)silane readily undergoes a diene condensation with cyclopentadiene and hexachlorocyclopentadiene[323-327]:

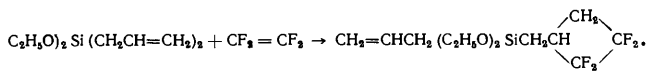


Allyldichloro(methyl)silane and 5,5-difluorotetrachlorocyclopentadiene[328,329] also undergo an analogous reaction[328,329], the latter reacting more readily than hexachlorocyclopentadiene. Alkenylsilanes containing hydrogen at the silicon undergo diene condensation with these compounds particularly readily.

Vinyl-containing organosilicon compounds undergo a Meerwein condensation with aryldiazonium halides[315]:



The reaction of alkenylsilanes with halogenoalkenes is also used for the preparation of halogeno-derivatives of organosilicon compounds[317,330]:



Organosilicon compounds with halogenated sulphur-containing organic groups are obtained by the reaction[331]:

$$p\text{-}ClC_6H_4SH + CH_2{=}CHSi(CH_3)(OC_2H_5)_2 \rightarrow p\text{-}ClC_6H_4SCH_2CH_2Si(CH_3)(OC_2H_5)_2.$$

The reaction takes place at 60°C under ultraviolet irradiation.

4. Organometallic Synthesis

Organometallic synthesis is widely used as a preparative method for obtaining various halogen-substituted organosilicon compounds with the halogen in a known position in the organic group bound to silicon.

The reaction of *p*-chlorophenylmagnesium bromide with silicon tetrachloride gives trichloro-*p*-chlorophenylsilane[332]. The reaction of *p*-chlorophenylmagnesium iodide with trichloro(methyl)silane gives dichloro-(*p*-chlorophenyl)methylsilane[333], that with chlorotrimethylsilane, *p*-chlorophenyltrimethylsilane[334]; that with trichlorosilane, dichloro-*p*-chlorophenylsilane[335]; that with trichloro(vinyl)-silane, dichloro-*p*-chlorophenylvinylsilane; and that with allyltrichlorosilane, allyldichloro-*p*-chlorophenylsilane[336]. *p*-Chlorophenylmagnesium bromide reacts analogously[154,333,336,337-341], but *o*-chlorophenylmagnesium bromide does not undergo these reactions[153]. A phenyl group with halogen in the *ortho*-position can be introduced in the reaction of *o*-halogenophenylmagnesium iodide with organohalogenosilanes[342]:

$$o\text{-}XC_6H_4MgI + (CH_3)_3SiCl \rightarrow o\text{-}XC_6H_4Si(CH_3)_3 + MgClI,$$

where X = Cl or F.

3-(*o*-Chlorophenyl)propylmagnesium bromide reacts with chlorotriphenylsilane by the reaction[343]:

$$o\text{-}ClC_6H_4[CH_2]_3MgBr + (C_6H_5)_3SiCl \rightarrow o\text{-}ClC_6H_4[CH_2]_3Si(C_6H_5)_3 + MgClBr.$$

Chlorobenzyl-substituted compounds are obtained in the reaction of organochlorosilanes with *o*- and *p*-chlorobenzylmagnesium chloride and *m*-chlorobenzylmagnesium bromide[344,345].

Polychlorophenylalkylchlorosilanes $C_6H_5 - {}_nCl_n(C_2H_5).SiCl_2$ [154,155] are obtained with the aid of an organomagnesium synthesis. Hexachlorobenzene, magnesium, and the corresponding halogenosilanes in tetrahydrofuran solution yielded perchlorophenyltrichlorosilane and alkylperchlorophenyldichlorosilanes[346].

p-Chlorophenylmagnesium bromide reacts with diethoxydiphenylsilane according to the reaction[347]

$$p\text{-}ClC_6H_4MgBr + (C_6H_5)_2Si(OC_2H_5)_2 \rightarrow p\text{-}ClC_6H_4(C_6H_5)_2SiOC_2H_5 + Mg(OC_2H_5)Br.$$

Fluorophenylmagnesium bromide reacts with silicon tetrachloride and alkylchlorosilanes to form trichloro-(fluorophenyl)silane[348] and alkyldichloro(fluorophenyl)silanes[349]. *p*-Fluorophenylmagnesium bromide reacts with trichloro(methyl)silane slowly, dichloro-(*p*-fluorophenyl)-methylsilane being formed. The reaction with difluorophenylmagnesium bromide is still more difficult, and as a result 2,4- and 3,5-$F_2C_6H_3(CH_3)SiCl_2$ are obtained. The reaction with dichlorodimethylsilane takes place more readily than that with trichloro(methyl)silane; triethoxy-(methyl)silane reacts even better with fluorophenylmagnesium bromides[350].

The production of fluoroaryl-substituted silanes by Grignard reaction has also been described[338,351,352]. Perfluorophenyl-substituted silanes[353], tetrakis-*m*-fluorobenzylsilane[354], and *m*-trifluoromethylphenyl-substituted silanes[328,348,354-358] were also obtained by this method.

Bromo-derivatives of aromatic and aliphatic-aromatic compounds with a known position of the bromine in the nucleus were obtained in an analogous manner[332,337,338,351,359-370].

Using organomagnesium compounds *p*-chlorophenyl- and *p*-bromophenylpentamethyldisilanes were obtained from pentamethyldisilane[49]. Mono- and di-substituted trifluoropropylchlorosilanes were obtained from $CF_3CH_2CH_2MgCl$ and $HSiCl_3$;[234] $(CF_3CH_2CH_2)_3SiH$ was obtained by the reaction of $HSiCl_3$ and $CF_3CH_2CH_2MgI$.[235]

Fully and partly fluorinated silanes[371-376], ω-chloroalkylsilanes[377,378] and halogen-containing acetylenic silanes[379] are obtained in an analogous manner.

Organolithium compounds are also widely used for obtaining halogenoaryl-substituted organosilicon compounds[190,380-382]. This method is especially effective for obtaining compounds containing rather large groups at the silicon atom. The reaction of *p*-bromophenyl-lithium with chlorotriphenylsilane gives *p*-bromophenyltriphenylsilane in 75% yield[383]. 3,5-Dibromophenyl-lithium reacts with silicon tetrachloride, trichloro(methyl)silane, and dichlorodimethylsilane[384] to form the corresponding dibromodiphenyl derivatives. Pentafluorophenyl-lithium and silicon tetrachloride gave tetrakisperfluorophenylsilane[385]; *m*-fluorophenyl-lithium and chloro(phenyl)silanes gave compounds of the formula $(m\text{-}FC_6H_4)_nSi(C_6H_5)_{4-n}$, where $n = 1-4$.[386]

Trimethyltribromomethylsilane was obtained from tribromomethyl-lithium and trimethylsilane[387]. *p*-Bromo and *p*-chloro-phenylethynyl-lithium react with silicon tetrachloride to form $(p\text{-}XC_6H_4C{\equiv}C)_4Si$, where X = Cl or Br.[388]

Organosodium synthesis was used for the introduction of chlorophenyl groups into bis(organochlorosilyl)-substituted benzenes[389]: the reaction of bromochlorobenzene with bis(phenyldichlorosilyl)benzene in the presence of sodium gave

$$[(ClC_6H_4)_2(C_6H_5)Si]_2C_6H_4;$$

$[(ClC_6H_4)_3Si]_2C_6H_4$ was obtained analogously from $(Cl_3Si)_2C_6H_4$.

5. Other Methods of Synthesis

Of the other methods for obtaining halogeno-derivatives of alkyl(or aryl)halogenosilanes and tetrasubstituted silanes, that of high-temperature condensation of alkyl and aryl halides with chlorosilanes is interesting. This reaction was first described in 1949[390,391] as applicable to the synthesis of alkyl- and alkenyl-silanes:

$$RX + HSiR'_3 \rightarrow RSiR'_3 + HX,$$

where R = alkyl or alkenyl group, and X = halogen. Subsequently it was used successfully for the synthesis of halogenoaryl substituted silanes.

The reaction can be effected in the liquid phase under pressure or in the gas phase at atmospheric pressure and 300–700°C. The reaction temperature can be greatly reduced by use of catalysts and initiators. These include halides of aluminium and of boron[392-394], aluminium oxide[390,395], palladium[396], benzoyl peroxide and ultraviolet light[226,397].

The reaction of dichlorobenzene and trichlorobenzene with trichlorosilane and dichloro(methyl)silane at 525°C in the vapour phase over palladium leads to the synthesis of the corresponding chloro- and dichloro-phenylchlorosilanes[396,398]. *p*-Dichlorobenzene reacts with chloro(methyl)phenylsilane[399] to form *p*-chlorophenylmethylphenylchlorosilane, and with chlorodimethylsilane[400] to form *p*-chlorophenyldimethylchlorosilane.

Hexafluorobenzene reacts with trichlorosilane to form dichlorofluoropentafluorophenylsilane and a mixture of isomers of bis(dichlorofluorosilyl)benzene[401].

The chloro-derivatives of thiophen (like thiophen itself) exhibit a much greater reactivity than benzene and its chloro-derivatives in condensation with silanes[402]. The condensation of silanes with 2,5-dichlorothiophen in the vapour phase at 570–580°C yielded 2-chloro-5-trichlorosilylthiophen and 2-chloro-5-dichloro(methyl)silylthiophen.

This method allowed the corresponding chloro(chlorovinyl)silanes to be obtained easily from dichloroethylene[85,210,400,403,404], trichloroethylene[85,210,398,405], and trichlorosilane, methyl- and ethyl-dichlorosilanes, chlorodimethylsilane, dichlorosilane, and chloro(methyl)silane.

The condensation of 1,3-dichlorobut-2-ene with dichlorosilane and trichlorosilane[406] gave respectively:

$$CH_3CCl{=}CHCH_2SiHCl_2 \text{ and } CH_3CCl{=}CHCH_2SiCl_3.$$

The reaction of silicon difluoride with hexafluorobenzene[407] gave trifluoro(pentafluorophenyl)silane $C_6F_5SiF_3$ and a mixture of the isomers of bis(trifluorosilyl)benzene.

The chloromethylation of benzylchlorodimethylsilane with CH_2O in fuming hydrochloric acid without a catalyst leads to the production of $ClCH_2C_6H_4CH_2Si(CH_3)_2Cl$; in the presence of $ZnCl_2$ chloromethylation is accompanied by side-processes[408]. The chloromethylation of the trialkyl(benzyl)silanes $R_3SiCH_2C_6H_5$ with 37% aqueous formalin solution and also with paraformaldehyde in CCl_4 and CH_3COOH leads to the formation of $CH_2ClC_6H_4CH_2SiR_3$.[409,410] With increase in the size of R the reaction becomes more difficult. Depending on the reaction conditions, different quantities of *p*-chloromethyl derivatives are formed; chloromethylation in water leads to the formation of > 90% of the *para*-isomer.

α-Methyltrimethylene oxide reacts with the chloroorganosilanes to form chloroalkoxy-derivatives[411]. The reaction of ethylene oxide with chloro(chloromethyl)methylphenylsilane, trichlorochlorophenylsilane, and chlorodichloromethyldimethylsilane gave the corresponding 2-chloroethoxysilanes[412].

The reaction of phosphorus(V) chloride with allyltrimethylsilane is interesting[413]:

$$(CH_3)_3SiCH_2CH{=}CH_2 + \overset{+}{P}Cl_4 \cdot \bar{P}Cl_6 \rightarrow (CH_3)_3SiCH_2CHClCH_2\overset{+}{P}Cl_3 \cdot \bar{P}Cl_6 \rightarrow \xrightarrow{SO_2} (CH_3)_3SiCH_2CHClCH_2P(O)Cl_2.$$

Tetrakis-(2,4,6-trichlorophenoxy)silane and tetrakis-(pentachlorophenoxy)silane are obtained from the corresponding phenoxides and silicon tetrachloride[414]. The reaction of chlorotriorganosilanes with $CH_2FCOONa$ and of triorganoethoxysilanes with $CH_2FCOONa$ gave halogen-substituted derivatives of the general formula $R_3SiOCOCH_2X$ (X = F or Br)[415].

On treating the carbinols $R_3SiC{\equiv}CR'R''OH$ with concentrated hydrochloric acid or sulphuryl chloride[416-418] the corresponding compounds with a chlorine atom in the organic group $R_3SiC{\equiv}CR'R''Cl$ are obtained.

An analogous reaction occurs between *p*-(2-hydroxyethyl)phenyltrimethylsilane and sulphuryl chloride in the presence of $CaCO_3$.[112]

On reacting with sulphuryl chloride, silicon-containing carboxylic acids are converted into the corresponding acid chlorides[419].

Chloromethyl-substituted organosilicon compounds can be obtained by the reaction[420]:

$$(C_2H_5OCH_2)_2Si(CH_3)R + 2 \cdot CH_3COCl \rightarrow (ClCH_2)_2Si(CH_3)R + 2 \cdot CH_3COOC_2H_5,$$

where R = CH_3 or C_3H_7.

Trichloro(phenyl)silane reacts with diazomethane[421] to form dichloro(chloromethyl)phenylsilane. Compounds of the general formula $(C_6H_5)_nSiCl_{4-n}$, where $n > 1$, do not undergo this reaction.

Triphenylsilyl-lithium reacts with halogenomethanes thus[422]:

$$(C_6H_5)_3SiLi + CH_nX_{4-n} \rightarrow CH_nX_{3-n}Si(C_6H_5)_3 + LiX,$$

where X = Cl, Br, or I, and $n = 0$, 1, or 2.

II. PROPERTIES

1. Reactions with Participation of the Halogen in the Organic Group

A halogen atom in the organic groups of organosilicon compounds is capable of taking part in nucleophilic substitutions [423-427].

α-Halogenoalkyl-substituted organosilanes are exceptionally inert towards electrophilic agents, but are considerably more reactive towards nucleophiles than the corresponding halogenohydrocarbons.

α-Chloro-derivatives are more reactive than γ-derivatives in most reactions. The reactivity of chlorine in compounds of the type $R_n(CH_3)_{3-n}SiCH_2Cl$ (R = C_6H_5, *p*-ClC_6H_4, $n = 1-3$) is considerably affected by the number of phenyl groups at the silicon atom; with increase in their number there is a sharp drop in the rate of substitution, owing to the steric effect of the phenyl groups [428].

Trialkyl-α-halogenosilanes are readily converted into the corresponding nitriles. Compounds of the general formula $R_nSi([CH_2]_xBr)_{4-n}$ react quantitatively in alcohol with NaCN and KCN to form $R_nSi([CH_2]_xCN)_{4-n}$; [429,430] with chloromethyl derivatives side reactions are observed (splitting). Cyanoalkyl-substituted organofluorosilanes are obtained by the same method [431]. By replacing bromine by the nitrile group in bromophenyl-substituted organoalkoxysilanes, cyanophenylorganoalkoxysilanes are obtained [432,433]. The replacement of bromine in the alkyl substituent in the aromatic ring takes place analogously [112]:

$$p\text{-}BrCH_2C_6H_4Si(CH_3)_3 + NaCN \rightarrow p\text{-}NCCH_2C_6H_4Si(CH_3)_3.$$

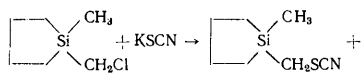
p-Bromophenyltrimethylsilane reacts with CuCn in the presence of pyridine [434]:

$$(CH_3)_3SiC_6H_4Br\text{-}p + CuCN \xrightarrow{C_5H_5N} (CH_3)_3SiC_6H_4CN\text{-}p.$$

$(NC)_2CHCH_2Si(CH_3)(OC_2H_5)_2$ was made from $CH_2I(CH_3)Si(OC_2H_5)_2$ and $NaCH(CN)_2$. [435] $CH_3(NC)_2CCH_2Si(CH_3)(OC_2H_5)_2$, which is more stable, was obtained in an analogous manner.

The nitriles obtained in this way can be easily converted into the corresponding amines, alcohols, and acids.

The halogen in an alkyl group can also be substituted by a thiocyanato-group, for example [436]:

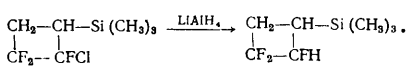


The chlorine atom in organic groups can be readily replaced by iodine [436-440]:

$$(CH_3)_3SiCH_2Cl + NaI \rightarrow (CH_3)_3SiCH_2I + NaCl.$$

In the reaction with KI the steric factor of the groups connected with the silicon plays an important part: $C_6H_5(CH_3)_2SiCH_2Cl$ and $(CH_3)_3SiOSi(CH_3)_2CH_2Cl$ react at only half the rate for $(CH_3)_3SiCH_2Cl$, [118,437] whereas $(C_6H_5)_3SiCH_2Cl$ does not react at all. [119] α-Halogenoalkylsilanes react with KI 3-5 times more rapidly than γ-halogenoalkyl-substituted silanes [423]. In the reaction with alkali metal halides chloroalkyl-substituted disilanes can be used successfully, for example, $ClCH_2(CH_3)_2SiSi(CH_3)_2CH_2Cl$ and $(CH_3)_3SiSi(CH_3)_2CH_2Cl$. [108]

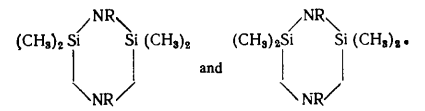
Under the action of $LiAlH_4$ halogen derivatives of tetrasubstituted silanes are hydrided [317]:



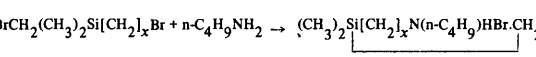
On treating halogenoalkylsilanes with $AgNO_2$ nitroso-derivatives are obtained, but on treatment with $NaNO_2$ nitro-derivatives—for γ-iodopropyltriethoxysilane $ONOCH_2CH_2CH_2Si(OC_2H_5)_3$ and $O_2NCH_2CH_2CH_2Si(OC_2H_5)_3$ respectively [441].

On heating $R_3SiCH_2C_6H_4CH_2Cl$ with $CaCO_3$ a chlorine atom is replaced by a hydroxyl group with the formation of $R_3SiCH_2C_6H_4CH_2OH$. [410]

The reaction of compounds of the type $R_3Si[CH_2]_nCl$ (n = 1 or 3) with ammonia or amines, organosilicon amines are formed [32,176,440,442-446]. A mixture of 2,6- and 2,5-disilapiperazines is formed in the reaction of bromomethylchlorodimethylsilane with primary amines or NH_3: [447]

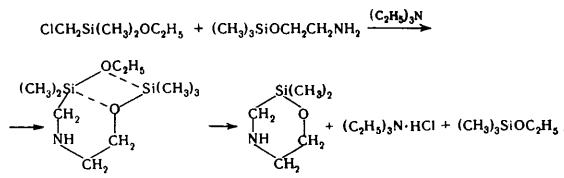


γ-Bromopropyl- and δ-bromobutyldimethyl(bromomethyl)silanes react with primary amines to form 3-sila-1-azacycloalkanes [448,449]:

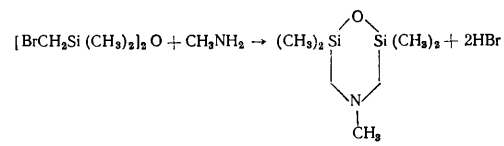


where x = 3 or 4.

α-Chloroalkylalkoxysilanes react with 2-(trimethylsiloxy)ethylamine [450]:



The reaction of 1,3-di(chloromethyl)-1,1,3,3-tetramethyldisiloxane with 2-aminoethoxytrimethylsilane yields 2,2,6,6-tetramethyl-4-(2-trimethylsiloxyethyl)-1-oxa-2,5-disila-4-azacyclohexane [451,452]. 1,3-Di(bromomethyl)-tetramethyldisiloxane reacts with methylamine to form 2,2,4,6,6-pentamethyl-2,6-disilamorpholine [447]:



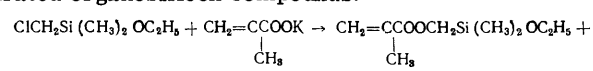
where X = halogen, R = alkyl.

Silylamines are obtained by treating halogenoalkyltrialkylsilanes with sodium acylamides [453,454]:

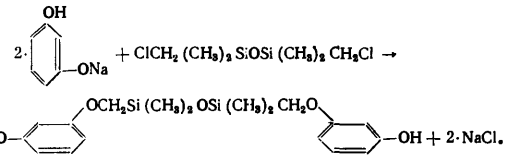
$$CH_3(R_2)SiCH_2X + CH_3CON(Na)C_2H_5 \rightarrow CH_3(R_2)SiCH_2N(C_2H_5)COCH_3 + NaX,$$

where X = halogen, R = alkyl.

In the reactions described above a halogen in the α-position to the silicon atom is more active than one in the γ-position. The reverse occurs in reactions with potassium acetate: greater activity is then exhibited by a halogen in the γ-position [455]. The synthesis of silicon-containing esters by this method has been studied often [420,436,456-459]. There is special interest in the reaction of halogenoalkyl-substituted silanes with salts of unsaturated acids, in particular methylacrylic acid, as a synthetic method for unsaturated organosilicon compounds:



In connection with this reaction mention must also be made of the reaction of chloromethylsiloxanes with monosodium and disodium salts of dihydric phenols[460]:



Silicon-containing esters are also obtained in the reaction of halogenoalkyl-substituted silanes with sodiomalonic and sodioacetoacetic esters[461-468] and also of chloromethylmethylalkoxysilanes with various acids in the presence of triethylamine[469].

Silicon-containing esters are used for obtaining organosilicon alcohols[57]:

$$R_3Si[CH_2)_nOCOCH_3 \xrightarrow[H_2SO_4]{CH_3OH} R_3Si[CH_2]_nOH.$$

γ-Chloroalkyltrialkylsilanes are more reactive than α-derivatives of also in reactions with the exchange of chlorine for an alkoxy-group under the action of sodium alkoxides on chloroalkyltrialkoxysilanes[470] and chloroalkyltrialkylsilanes[471]. Cellulose ethers are also obtained by this reaction—triethylsilylmethyl cellulose and trimethylsilyl methyl cellulose

$$[C_6H_7O_2(OH)_{3-x}(OCH_2SiR_3)_x]_n,$$

where R = CH_3 or C_2H_5.[472]

In these reactions, in addition to the replacement of chlorine by an ester group there is splitting of the Si–C bond[9,10], which increases with increase in the length of the radical in the sodium alkoxide[473].

A study of the reaction of halogenoalkylchlorosilanes with aromatic hydrocarbons in the presence of Friedel–Crafts catalysts[31,474-479] showed that β- and γ-chloroalkylchlorosilanes are more reactive than α-chloro-substituted ones. The reactivity increases with replacement of chlorine at a silicon atom by alkyl groups. These reactions are used for obtaining various aliphatic-aromatic chlorosilanes. The mechanism of this reaction for the α-chloroalkyl-substituted silanes can be represented as follows[475]:

$$Cl_2(C_2H_5)SiCHClCH_3 \xrightarrow{AlCl_3} Cl_2(C_2H_5)\overset{+}{S}iCHCH_3 + [AlCl_4]^- \rightarrow$$

$$\rightarrow Cl_2(C_2H_5)SiCH_2\overset{+}{C}H_2 + [AlCl_4]^- \xrightarrow{-C_6H_6} Cl_2(C_2H_5)SiCH_2CH_2C_6H_5 + AlCl_3 + HCl.$$

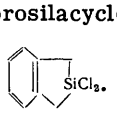
γ-Chloroalkyl-substituted derivatives react according to the scheme[478]:

$$Cl_3SiCH_2CH_2CH_2Cl \xrightarrow[C_6H_6]{AlCl_3} Cl_3SiCH_2\underset{CH_3}{CHC_6H_5} + Cl_3Si(CH_2)_3C_6H_5.$$

Compounds with halogenoacyl group can be used as acylating agents[480]:

$$(CH_3)_3SiC_6H_5COCl + C_6H_5CH_3 \rightarrow (CH_3)_3SiC_6H_5COC_6H_5CH_3\text{-}p + HCl.$$

The action of $AlCl_3$ on chloromethylbenzyldichlorosilane gives 3 : 4 benz-1,1-dichlorosilacyclopentane[481]:



The silylalkylation of aromatic hydrocarbons by dichloromethylchlorosilanes proceeds normally, but for $\alpha\alpha$-, $\beta\beta$-, and $\alpha\beta$-dichloroalkyl-substituted compounds is complicated by the reduction of one C–Cl bond by hydrogen.

Attention has recently been attracted to the high-temperature condensation of (chloroaryl)chlorosilanes with organochlorosilanes, leading to the formation of bis(organochlorosilyl)-substituted benzenes[399,482-484]:

$$Cl_{3-n}R_nSiC_6H_4Cl + HSiR'_mCl_{3-m} \rightarrow Cl_{3-n}R_nSiC_6H_4SiR'_mCl_{3-m}.$$

The condensation can proceed both in the liquid and in the vapour phase and is accompanied by several side-reactions. For example, in the reaction of chlorophenylalkylchlorosilanes with alkylchlorohydrosilanes the main reaction is accompanied by the following reactions[485]:

$$Cl_{3-n}R_nSiC_6H_4Cl + HSiR_mCl_{3-m} \rightarrow Cl_{3-n}R_nSiC_6H_5 + SiR_mCl_{4-m},$$

$$HSiR_mCl_{3-m} + HCl \rightarrow SiR_mCl_{4-m} + H_2,$$

$$Cl_{3-n}R_nSiC_6H_4SiR_mCl_{3-m} + HCl \rightarrow Cl_{3-n}R_nSiC_6H_5 + SiR_mCl_{4-m}.$$

Halogenosilanes other than chlorosilanes are also used in condensation, for example, chlorophenyltrifluorosilane[486].

In the gas-phase condensation of trichlorosilane and dichloro(methyl)silane with $ClC_{10}H_8SiCl_3$ (mixture of isomers), bis(organochlorosilyl)naphthalenes are formed[487].

In the action of nucleophilic and electrophilic reagents on halogenoalkylchlorosilanes, as well as cleavage of the Si–C bond, loss of hydrogen halide also takes place leading to the formation of halogenosilanes with alkenyl radicals.

A systematic study of this reaction[61,82,83,86,101,102,170,171,248,274,298,488-508] led to the finding and formulation of the principal regularities[509] and to the determination of the boundary of applicability of the various dehydrohalogenating agents in this reaction.

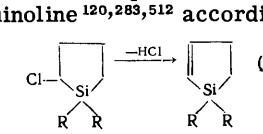
The ease of loss of HCl from the monochloroalkylchlorosilanes depends on the position of chlorine relative to the silyl group and decrease in the order $\beta > \alpha > \gamma$. The HCl is removed from secondary α- and β-chloroalkyl groups more readily than from primary groups. HBr is lost more readily than HCl. In the stepwise replacement of alkyl groups for chlorine the β-decomposition of the compounds of the type $R_3SiCH_2CH_2Cl$ gives way to dehydrochlorination.

Quinoline, isoquinoline, and piperidine dehydrochlorinate compounds with any silyl groups, but with quinoline the removal of HCl takes place successfully only from β-chloroalkyl groups, whereas catalytic amounts of piperidine are capable of bringing about the loss of HCl also from γ-chloroalkyl and chloroacyl groups. In the dehydrochlorination of $\beta\gamma$-dichloropropyltrichlorosilane under the action of $AlCl_3$ γ-chloroallyltrichlorosilane is formed; in the dehydrochlorination by quinoline $Cl_3SiCH{=}CHCH_2Cl$ and $Cl_3SiCH_2CH{=}CHCl$ are formed in approximately equal amounts[510].

In the dehydrochlorination of 1-phenyl-2-trichlorosilyl-1,2-dichloroethane and 1-phenyl-1-trichlorosilyl-1,2-dichloroethane in the presence of $AlCl_3$, 1-phenyl-2-chlorovinyltrichlorosilane is formed[511].

Chloropolychloroalkylsilanes are dehydrochlorinated by quinoline much more readily than the monochloro-derivatives.

Silacycloalkanes are dehydrochlorinated on heating and also in the presence of quinoline and *N*-methyl-1,2,3,4-tetrahydroquinoline[120,283,512] according to the reaction:



Unlike the 2-chloro-substituted, 1,1,3-trichlorosilacyclopentane is converted under analogous conditions into 3-butenyltrichlorosilane. The dehydrobromination of 2-bromo-1,1,2-triphenyl-1-silacyclobutane leads to the formation of 1,1,2-triphenyl-1-silacyclobut-2-ene[140].

The dehydrobromination of 2-cyanobromoethyltrichlorosilane by quinoline gives β-cyanovinyltrichlorosilane [139]. The dehydrochlorination of $R_3SiCH_2SCHClCH_3$ gives $R_3SiCH_2SCH{=}CH_2$. [513]

A reaction very similar to the dehydrohalogenation considered above is dehalogenation, leading to the formation of silyl-substituted compounds of the ethylene and acetylene type [514]. For example:

$$(Cl_3SiCCl_2)_2 \xrightarrow{-Cl_2} Cl_3SiCCl{=}CClSiCl_3.$$

On further dehalogenation, $Cl_3SiC{\equiv}CSiCl_3$ is formed. The reaction occurs at a temperature above 100°C in the presence of copper.

Metallic zinc can also be used as a dehydrochlorinating and dehalogenating agent. The ease of removal of halogens then decreases in the order: I > Cl > Br [229,317,515]; fluorine is not lost. For example [229]:

$$CF_2ClCFClCH_2CHISi(CH_3)_3 \xrightarrow[(C_4H_9)_2O]{Zn} CF_2{=}CFCH{=}CHSi(CH_3)_3.$$

Di-(iodomethyl)dimethylsilane is reduced to tetramethylsilane [38]:

$$(CH_3)_2Si(CH_2I)_2 \xrightarrow[C_3H_6OH]{Zn} (CH_3)_4Si.$$

$AlCl_3$ can be used for the dehydrochlorination only of compounds with trichlorosilyl groups; in other instances there is either decomposition or rearrangement of the organosilicon compounds. The rearrangement consists of the migration of an alkyl group from a silicon to a carbon atom [265]. For example [516]:

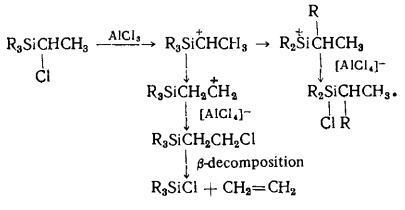
$$(CH_3)_3SiCH_2Cl \xrightarrow{AlCl_3} C_2H_5(CH_3)_2SiCl.$$

The mechanism of this reaction can be represented as follows:

$$(CH_3)_3SiCH_2Cl \xrightarrow{AlCl_3} (CH_3)_3\overset{+}{S}iCH_2 + [AlCl_4]^- \rightarrow$$

$$\rightarrow (CH_3)_2\overset{+}{S}iCH_2CH_3 + [AlCl_4]^- \rightarrow C_2H_5(CH_3)_2SiCl + AlCl_3.$$

For α-chloroethyltriorganosilane the reaction proceeds in two directions [103]:



For dichloromethyltrimethylsilane α-chloroethyldimethylchlorosilane is formed in the first stage, and then rearranges according to the scheme given above:

$$(CH_3)_3SiCHCl_2 \xrightarrow{AlCl_3} (CH_3)_2\underset{Cl\ Cl}{SiCHCH_3} \rightarrow (CH_3)_2SiCl_2 + CH_2{=}CH_2.$$

$AlCl_3$ also catalyses the migration of trimethylsilyl and dimethylchlorosilyl groups [87,517]:

$$\begin{matrix}(CH_3)_nSiCl_{3-n}\\ |\\ (CH_3)_2SiCH_2Cl\end{matrix} \xrightarrow{AlCl_3} (CH_3)_2\overset{Cl}{\underset{|}{Si}}CH_2Si(CH_3)_nCl_{3-n}.$$

Chloromethylpentamethyldisilane undergoes an analogous rearrangement in the presence of sodium ethoxide [108] with the formation of $(CH_3)_3SiCH_2Si(CH_3)_2OC_2H_5$.

Di(chloromethyl)tetramethyldisilane rearranges under the action of $AlCl_3$ into $(CH_3)_3SiCHClSi(CH_3)_2Cl$ or $\{Cl(CH_3)_2Si\}_2CHCH_3$, depending on the conditions [108].

1-Chloromethyl-1-methylsilacyclopentane rearranges into 1-chloromethyl-1-methylsilacyclohexane under the action of $AlCl_3$. [436]

Chloro- and bromo-alkyltriorganosilanes (with the exception of β-halogeno-derivatives) readily form the corresponding organo-magnesium and -lithium compounds, which are capable of all the reactions peculiar to Grignard reagents [205,518,519]. There is a report [520] of the preparation of organomagnesium compounds of the type $R_3SiO[CH_2]_nMgCl$ (where R is alkyl or phenyl; $n = 4$ or 5). Organomagnesium compounds can also be obtained from halogenomethyl-substituted organocyclosiloxanes [521] and disilanes [108].

Organosilicon compounds which contain a halogen in the aromatic nucleus directly connected with silicon directly or through alkyl groups form organo-magnesium and -lithium compounds in high yields [351,368,382,387,410,480,522-528].

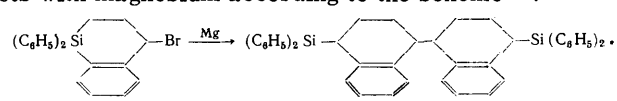
The formation of organolithium compounds is greatly influenced by the steric effect of organic groups bound to the silicon atom. Chloromethyltrimethylsilane readily forms trimethylsilylmethyl-lithium [529,530]:

$$ClCH_2Si(CH_3)_3 + 2Li \rightarrow LiCH_2Si(CH_3)_3 + LiCl.$$

However, organolithium compounds could not be obtained from chloromethyldimethylphenylsilane [531]. γ-(*o*-chlorophenylpropyltriphenylsilane also does not react with lithium. However, all these compounds readily form organomagnesium derivatives.

p-Chlorophenyldimethylsilane forms organo-lithium and -magnesium compounds [532]; $p\text{-}LiC_6H_4Si(CH_3)_2H$ readily condenses with the formation of oligomers with phenylenesilyl units.

4-Bromo-2,3-benz-1,1-diphenyl-1-silacyclobutane reacts with magnesium according to the scheme [201]:



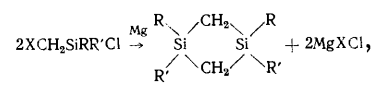
With mercury(II) chloride, organomagnesium compounds can be readily converted into organomercury compounds [92,108,471,531,533]:

$$ClMgCH_2Si(CH_3)_2R + HgCl_2 \rightarrow (CH_3)_2Si(R)CH_2HgCl.$$

Halogenoalkyl(or aryl)silanes which contain reactive atoms or groups (halogen, OR) do not form Grignard reagents. Reactions between γ-chloroalkylchlorosilanes and magnesium lead to the formation of silacyclobutanes [214,534,535]:

$$ClCH_2CH_2CH_2SiRCl_2 \xrightarrow{Mg} \overline{CH_2CH_2CH_2SiRCl}$$

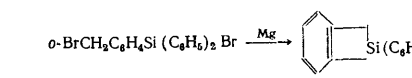
Halogenomethyldialkylchlorosilanes react with magnesium in ether or tetrahydrofuran with the formation of disilacyclobutanes [536-540]:



where X = Cl or Br; R and R′ = CH_3 or C_6H_5.

Under the same conditions $BrR_2SiCH_2SiR_2CH_2SiR_2CH_2Cl$ is converted into 1,3,5-trisilacyclohexane [541].

o-Bromomethylphenyldiphenylbromosilane reacts under the same conditions with magnesium with the formation of 2:3-benz-1,1-diphenyl-1-silacyclobut-2-ene [200]:



Halogenomethyltriorganosilanes react with sodium to form 1,2-triorganosilyl-substituted ethanes[542,543]:

$$2\cdot(CH_3)_3SiCH_2Br \xrightarrow{Na} (CH_3)_3SiCH_2CH_2Si(CH_3)_3.$$

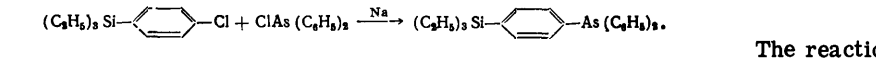
When there is common condensation of halogenoalkyl-substituted silanes and triorganohalogenosilanes with sodium the reaction is[544]:

$$(CH_3)_3SiCCl{=}CH_2 + ClSi(CH_3)_3 \xrightarrow{Na} [(CH_3)_3Si]_2C{=}CH_2.$$

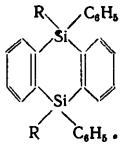
Several disila-alkenes were obtained by this method[545]. The use of bifunctional compounds in this reaction leads to the formation of silacycloalkanes. For example, $Br(CH_3)_2SiCH_2Si(CH_3)_2CH_2Si(CH_3)_2Br$ and $(CH_3)_2Si(CH_2Cl)_2$ react with sodium to form a ring of composition $[Si(CH_3)_2CH_2]_4$.[531]

Silacyclopropane, which is formed in the reaction of $RR'Si(CH_2Cl)_2$ with sodium–potassium alloy (at 260–280°C in a stream of helium) is unstable and readily rearranges into $R'RSiH(CH{=}CH_2)$.[548] When chloro(chloromethyl)dimethylsilane and dichlorodimethylsilane react with magnesium, zinc or alkali metals, ωω′-dichloropoly(dimethylmethylenes) are formed[519]; *m*- and *p*-halogenophenyldiorganochlorosilanes react with finely divided sodium or magnesium to form silylphenylene polymers of linear structure[547].

Condensation with sodium can be used for the replacement of halogens in an organic group, for example, by arsenic[337]:

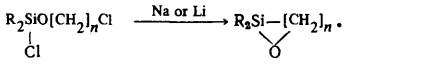


Reaction of ω-(*o*-chlorophenyl)alkyldiorganosilanes with sodium leads to the formation of 2:3-benz-1-silacycloalkanes[548]. $o\text{-}ClC_6H_4Si(R)(C_6H_5)H$ reacts with sodium[549] with the formation of *cis*- and *trans*-isomers:



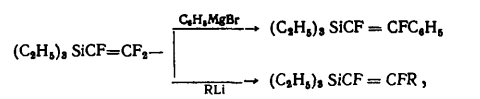
γ-(*o*-Chlorophenyl)propyltriphenylsilane reacts with sodium with loss of a phenyl group and formation of 2:3-benz-1,1-diphenylsilacyclohex-2-ene[343]. This reaction does not take place with lithium, but the same results can be obtained by the reaction of γ-(*o*-chlorophenyl)propyldiphenylsilane with lithium.

Halogenoalkoxy-substituted organochlorosilanes are converted into cyclic compounds under the action of sodium or lithium, according to the reaction[550]:



α- and β-chloroalkyltrichlorosilanes react with organomagnesium compounds differently: $CH_3CHClSiCl_3$ and CH_3MgBr form the corresponding trimethyl derivative, but $ClCH_2CH_2SiCl_3$ undergoes β-decomposition with formation of tetramethylsilane and ethylene only[173]. There are no side reactions in alkylation by Grignard reagents of α-, γ-, and δ-chloroalkylchlorosilanes. It was subsequently established[551] that the reaction of $ClCH_2CH_2SiCl_3$ with a Grignard reagent takes place through trialkylchlorosilanes which are formed as a result of β-decomposition; the latter, by reacting with the Grignard reagent, form the tetraalkylsilanes. There is simultaneous reaction at the C–Cl bond, hence the β-halogenoalkyltrichlorosilanes are capable of undergoing the usual Grignard–Wurtz reaction[292,293], the yield of products thus obtained depends on the nature of both reagents. This reaction enabled the chlorine in the trichlorosilyl group to be partially replaced by organic groups[552].

Perfluorovinyltriorganosilanes react readily with organo-magnesium and -lithium compounds with replacement of the fluorine in the β-position by organic groups[553]:

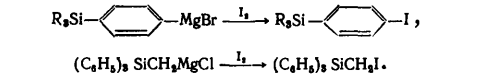


where R = C_6H_5, $CH_2{=}CH$, $CH_2{=}CH{-}CH_2$, or C_4H_9.

Halogenomethyl-substituted organohalogenosilanes react with organomagnesium compounds with replacement of the halogen in the methyl group[119,554]:

$$CH_3Si(Cl_3)\,CH_2Cl + 2RMgI \rightarrow R_2(CH_3)\,SiCH_2I + MgCl_2 + MgClI,$$

Similar results are obtained in the reaction with organomagnesium halides of compounds obtained on the basis of halogenoalkyl(or aryl)-substituted silanes[555]:



$$(C_6H_5)_3SiCH_2MgCl \xrightarrow{I_2} (C_6H_5)_3SiCH_2I.$$

The introduction of a halogen into an ethynyl group is based on the same method[556]:

$$R_3SiC{\equiv}CH \xrightarrow{R'MgBr} R_3SiC{\equiv}CMgBr \xrightarrow{Br_2} R_3SiC{\equiv}CBr.$$

The reaction of trichloromethyltrimethylsilane with methylmagnesium bromide proceeds with loss of the trichloromethyl group[557].

Chloro-substituted silacyclopentanes react with CH_3MgI differently depending on the position of the chlorine in the ring[283]: 1,1,2-trichlorosilacyclopentane reacts with replacement of the chlorine atoms at the silicon atom by methyl groups with the formation of 1,1-dimethyl-2-chlorosilacyclopentane, whereas 1,1,3-trichlorosilacyclopentane undergoes rearrangement under the action of CH_3MgI with the formation of 3-butenyltrichlorosilane, which is methylated by methylmagnesium iodide, being converted into $CH_2{=}CHCH_2CH_2Si(CH_3)_3$.

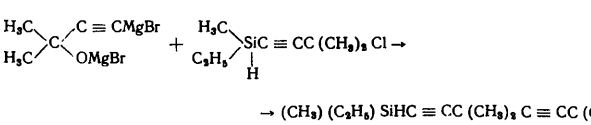
In the reaction of halogen derivatives of organohalogenosilanes with Iotsich reagent, first there is replacement of halogen connected with silicon atoms[558]; for example, $(CH_3)_2(CH_2Cl)SiCl$ and $HOC(R)(R')C{\equiv}CMgX$ give:

$$HOC(R)(R')C{\equiv}CSi(CH_3)_2CH_2Cl.$$

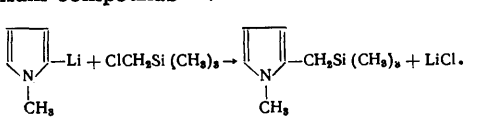
Halogen derivatives of tetrasubstituted silanes react at the halogen atom with entry into the organic group[418]:

$$R_3SiC{\equiv}CC(CH_3)_2Cl + XMgC{\equiv}CC(CH_3)_2OH \rightarrow$$
$$\rightarrow R_3SiC{\equiv}CC(CH_3)_2C{\equiv}CC(CH_3)_2OH + MgClX.$$

This reaction is widely used for obtaining organosilicon alcohols of the diacetylene series[559–562]. For example,



Silylmethylpyrroles have been obtained with the aid of organolithium compounds[563]:

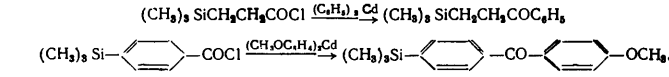


It has been reported[564] that in the reaction of chloromethyltrimethylsilane with butyl-lithium trimethylsilylcarbene $(CH_3)_3SiCH$ is formed, which on recombination gives

$$(CH_3)_2SiCH = CHSi(CH_3)_3.$$

Organosilicon acyl halides react with organocadmium compounds to form the corresponding ketones[110,480]:

$$(CH_3)_3SiCH_2CH_2COCl \xrightarrow{(C_6H_5)_2Cd} (CH_3)_3SiCH_2CH_2COC_6H_5$$



Halogenoalkyl-substituted silanes react with organic derivatives of phosphoric and phosphinic acids.

The Arbuzov rearrangement of $P(OC_2H_5)_3$ [565] and $C_6H_5P(OC_2H_5)_2$ [566] with $R_n(R'O)_{3-n}Si[CH_2]_XCl$ was used to synthesise compounds of the general formula

$$R_n(R'O)_{3-n}Si[CH_2]_xP\cdot(O)(R'')OC_2H_5.$$

where R and R′ are alkyl groups and R″ is C_6H_5 or OC_2H_5.

Chloromethyltrialkylsilanes react with R_3P [567,568] to form phosphonium salts:

$$R'_3SiCH_2Cl + R_3P \longrightarrow (R'_3SiCH_2PR_3)^+Cl^-$$

which on pyrolysis are converted into $R'_3SiCH{=}PR_3$.

Trialkylsilyl-substituted alkylphosphinic acids are obtained by the reactions[569,570]:

$$R_3Si[CH_2]_nCl + (R'O)_3P \xrightarrow{(t\text{-}C_4H_9O)_2} R_3Si[CH_2]_nP(O)(OR')_2 + R'Cl,$$

where R and R′ are alkyl groups and $n = 1$ or 3. The reaction with $(C_6H_5)_2POC_2H_5$ takes place analogously[570,571].

Dialkyl(triorganosilylmethoxymethyl) phosphinates are obtained in the reaction of dialkyl(sodioxymethyl) phosphinates with chloromethyltriorganosilanes[572,573]:

$$R_2P(O)CH_2ONa + ClCH_2SiR'_3 \longrightarrow R_2P(O)CH_2OCH_2SiR'_3 + NaCl.$$

Compounds of the formula $(RO)_2P(O)CH_2ONa$, [574] phosphine oxides, and their alkali metal salts[575] can be used in this reaction.

The chlorine in the chloromethyl group can also be replaced by residues of dialkyl(or aryl)dithiophosphonic (or dithiophosphinic) acids[576]. Chloropropylmethyldiethoxysilane is used for the production of γ-mercaptopropylmethyldiethoxysilane[577].

Bromomethyl-γ-bromopropyldimethylsilane reacts with Na_2S to form 3-sila-1-thiocyclohexane[448]:

$$BrCH_2Si(CH_3)_2CH_2CH_2CH_2Br + Na_2S \rightarrow (CH_3)_2\overline{SiCH_2CH_2CH_2SCH_2} + 2\,NaBr.$$

3-Sila-1-thiocycloheptane is obtained analogously from the δ-bromobutyl-derivative of silane[449].

Heterocycles containing silicon and sulphur are also obtained by the reaction[578]:

$$[ClCH_2(CH_3)_2Si]_2NH + 2H_2S \xrightarrow{(C_2H_5)_3N}$$

$$\rightarrow (CH_3)_2\overline{SiSSi(CH_3)_2CH_2SCH_2} + NH_4Cl + (C_2H_5)_3N\cdot HCl.$$

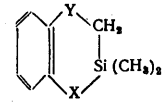
1,3-Bis(chloromethyl)tetramethyldisiloxane reacts with KSH to form 2,2,6,6-tetramethyl-1-oxa-4-thio-2,6-disilacyclohexane[579].

Chloromethyldimethylchlorosilane reacts with thiols[580]:

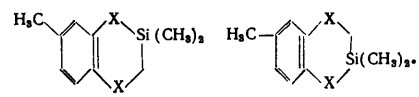
$$ClCH_2(CH_3)_2SiCl + HS[CH_2]_nSH \rightarrow (CH_3)_2\overline{SiS[CH_2]_nSCH_2} + 2HCl,$$

where $n = 2$ or 3.

Chloro(chloromethyl)dimethylsilane in the presence of triethylamine reacts with compounds of the general formula $o\text{-}HXC_6H_4YH$ (where X = O or NH and Y = O, NH, or S)[581] to form



The reaction of chloro(chloromethyl)dimethylsilane with $3,4\text{-}(HX)_2C_6H_3CH_3$ (where X = O or S)[582] in an analogous manner to form a mixture of compounds corresponding to the formulae:



Chloromethyl-containing organosilicon alcohols undergo intramolecular condensation on heating[448,449]:

$$ClCH_2(CH_3)_2Si[CH_2]_nOH \rightarrow (CH_3)_2\overline{Si[CH_2]_nOCH_2} + HCl,$$

where $n = 3$ or 4.

2. Reactions which Do Not Involve a Halogen in an Organic Group

Halogen-substituted organohalogenosilanes, according to the reactivity of the halogens connected with silicon, in reactions with nucleophilic reagents surpass the analogous compounds which do not contain a halogen in an organic group. The Si–Cl bond is more reactive than the C–Cl bond, therefore the action of nucleophilic reagents is directed towards it first[583]. The reactivity of the halogen connected with silicon is also greatly affected by the type and number of the organic groups at the silicon. Chloro(chloromethyl)methylsilanes can be arranged in the following series according to reactivity[584]:

$$CHCl_2Si(CH_3)_2Cl < CH_2ClSi(CH_3)_2Cl < CH_2ClSi(CH_3)Cl_2.$$

In the esterification of halogenoalkyl(or aryl)halogenosilanes the corresponding halogenoalkyl(or aryl)alkoxyderivatives are formed, for example, halogenoalkylethoxysilanes[17,18,184,377], halogenoarylethoxysilanes[180,187], and halogenocycloalkylethoxysilanes[184,186]. In partial esterification under mild conditions (in the presence of hydrogen chloride at reduced temperature) halogenoalkylalkoxychlorosilanes can be isolated, for example, chloromethylmethylethoxychlorosilane[539], γγγ-trifluoropropylmethylethylethoxychlorosilane[585]. The basicity of trimethylethoxysilane decreases regularly as the methyl groups are replaced by γγγ-trifluoropropyl groups[586,587].

In the hydrolysis of trifluoropropylchlorosilanes $(CF_3CH_2CH_2)_nSiCl_{4-n}$ the products obtained[231,235] are $(R_3Si)_2O$ ($n = 3$), $(R_2SiO)_X$ ($n = 2$), and $(RSiO_{1.5})_X$ ($n = 1$), where $R = CF_3CH_2CH_2$. The hydrolysis of γγγ-trifluoro-α-chloropropylmethyldichlorosilane and γγγ-trifluoro-β-chloropropylmethyldichlorosilane leads to the formation of linear and cyclic siloxanes of composition[77]:

$$[CF_3CH_2CHClSi(CH_3)O]_n \text{ and } [CF_3CHClCH_2Si(CH_3)O]_n.$$

Disiloxanes are obtained by hydrolysis of bromophenylmethylvinylchlorosilane[588] and trifluoropropylmethylchlorosilanes of formula[585]:

$$(CF_3CH_2CH_2)_n(CH_3)_{3-n}SiCl,$$

and also acyloxy-derivatives[589,590] of formula

$$(p\text{-}XC_6H_4)_3SiOCOR,$$

where X = halogen.

In the hydrolysis of γγγ-trifluoropropylmethyldichlorosilane and the subsequent catalytic destruction of the moist hydrolysate in a vacuum in the presence of catalytic amounts of alkali[580,591,592], two stereoisomers of 1,3,5-tris-(γγγ-trifluoropropyl)-1,3,5-trimethylcyclotrisiloxane are isolated.

Under the same conditions, cyclic trimer and cyclic tetramer were isolated[239] from a hydrolysate of general formula

$$[CHF_2CH_2CH_2(CH_3)_n \times SiO_{\frac{3-n}{2}}]_x$$

and cyclic tri-, tetra-, and penta-siloxanes were isolated from a mixture of $(CH_3)_2SiCl_2$ and $CF_3CH_2CH_2(CH_3)SiCl_2$.[593] On heating bis-(γγγ-trifluoropropyl)diethoxysilane with dilute HCl, $[(CF_3CH_2CH_2)_2SiO]_4$ was obtained, which on heating in the presence of a little KOH rearranges into a cyclic trimer[594].

Chloromethylmethylcyclosiloxanes with three and four siloxane units were obtained by the hydrolysis of ωω′-dichloro(chloromethyl)methylpolysiloxanes ($n = 1-5$).[595]

On treatment of $ClCH_2(CH_3)SiCl_2$ and $BrCH_2(CH_3)SiCl_2$ with a mixture of ether, acetone, aniline, and water, chloro- and bromo-methylethyldihydroxysilanes are obtained[596]; chloromethyldimethylhydroxysilane is obtained by hydrolysis of 1,3-dichloromethyltetramethyldisilazane[597]. In the hydrolysis of an ethereal solution of $C_6H_3Cl_2Si(OCOCH_3)_3$ with water[598] the monomer $C_6H_3Cl_2Si(OH)_3$ is isolated. Under analogous conditions $(p\text{-}ClC_6H_4)_2Si(OH)_2$ and $(p\text{-}BrC_6H_4)_2Si(OH)_2$[599,600] are obtained, and also a compound of the formula

$$R_{n-3}(p\text{-}XC_6H_4)Si(OH)_n,$$

where R = CH_3 or C_6H_5; X = Cl or Br and $n = 1$ or 2[601].

In the hydrolysis of m- and p-$XC_6H_4Si(CH_3)_2Y_2$ (where X = Cl or Br and Y = Cl or OCH_3)[602] the corresponding m- and p-$XC_6H_4Si(CH_3)(OH)_2$ are obtained.

$(p\text{-}XC_6H_4)_2Si(OH)_2$, where X = Cl or F, were obtained by hydrolysis of the corresponding organochlorosilanes in the presence of $(NH_4)_2CO_3$ at 0°C.[603,604]

ωω-Dihydroxy(chloromethyl)methylpolysiloxane oligomers with two, three, and four siloxane units were obtained by the hydrolysis of the corresponding ωω-dichloro-containing compounds[595].

The nature of the substituent at the silicon atom has a considerable effect on the acid properties of organohydroxysilanes: the introduction of halogen into alkyl[605] and aryl[604] groups increases the acidity.

The rate of polycondensation of halogenomethylmethyldihydroxysilanes is considerably less than that for dimethylhydroxysilane[606]; in particular, chloromethylmethyldihydroxysilane is condensed at less than one-thirtieth the rate of dimethyldihydroxysilane[607].

Chloromethyldimethylhydroxysilane reacts with dimethyldichlorosilane in the presence of triethylamine to form 1,5-bis(chloromethyl)hexamethyltrisiloxane[608].

In the reactions of halogenated organohalogenosilanes with organometallic compounds, first of all the halogen at the silicon atom is replaced by organic groups[77,202,485,609]. Halogenoaryl silanes react with organolithium compounds with replacement of a hydrogen atom by an organic group[343]:

$$o\text{-}ClC_6H_4[CH_2]_3Si(C_6H_5)_2H + C_6H_5Li \rightarrow o\text{-}ClC_6H_4[CH_2]_3Si(C_6H_5)_3 + LiH.$$

Chloromethylorganodichlorosilanes react with organomagnesium compounds from ωω-dibromoalkanes, forming silacycloalkanes[438,610]:

$$CH_2Cl(CH_3)SiCl_2 + BrMg[CH_2]_4MgBr \rightarrow \square Si\begin{matrix}CH_3\\CH_2Cl\end{matrix} + 2MgClBr.$$

In the hydrogenation of chloromethylchlorosilanes of the type

$$CH_{3-n}Cl_nSiCl_3[611] \quad \text{or} \quad CH_2ClSiR_{3-n}Cl_n[448],$$

the corresponding silicon hydrides are formed. In the hydrogenation of organochlorosilanes with trifluoropropyl groups[235,237], compounds of the formula $(CF_3CH_2CH_2)_n.SiH_{4-n}$ are obtained. The action of $LiAlH_4$, on $Cl_3SiCCl_2.SiCl_3$ yielded $H_3SiCCl_2SiH_3$,[87] which explodes when heated in a vacuum.

Chloromethyldimethylchlorosilane reacts with ammonia to form a silazane[578]:

$$ClCH_2(CH_3)_2SiCl + NH_3 \rightarrow [ClCH_2(CH_3)_2Si]_2NH + HCl.$$

The main products of the ammonolysis of $CF_3CHFCH_2Si.(CH_3)Cl_2$ are

$$[CF_3CHFCF_2(CH_3)(NH_2)Si]_2NH$$

and cyclosilazanes[612].

In the reaction of chloroalkylorganochlorosilanes with KHF_2 fluorine replaces chlorine attached to silicon[245]:

$$ClCH_2CH_2CH_2Si(C_2H_5)Cl_2 + KHF_2 \rightarrow ClCH_2CH_2CH_2Si(C_2H_5)F_2.$$

Halogeno-organochlorosilanes react with anhydrides and salts of organic acids[613,614] and with salts of difluorophosphoric acid[615] according to the reactions:

$$R_3SiCl + (R'CO)_2O \rightarrow R_3SiOCOR' + R'COCl,$$

$$R_3SiCl + HCOONa \rightarrow R_3SiOCOH,$$

$$RR'_2SiCl + NH_4OP(O)F_2 \rightarrow RR'_2SiOP(O)F_2 + NH_4Cl,$$

where R = p-XC_6H_4 (X = Cl, Br, F), R′ = H, CH_2, C_2H_5, $CH_{3-n}Cl_n$.

Halogenoalkyl(or aryl)silanes react with alcohols in the presence of sodium alkoxides[616,617] or H_2PtCl_6[249] with the formation of alkoxysilanes; they are readily halogenated at the Si–H bond by the action of halides[613,614,617-620] or phosphorus(V) chloride[200].

The presence of electrophilic halogenoalkyl substituents in silane is responsible for the considerable retardation of the halogenation (in comparison with organosilanes, which do not contain halogen atoms in the organic groups)[620]. The reactivity of $ClC_6H_4SiH_3$ in reactions with RCOOH is greater than that of $C_6H_5SiH_3$.[621] The condensation of tri-p-chlorophenylsilane with alkyl chlorides, alkenyl chlorides, chlorobenzene, and p-dichlorobenzene proceeds with higher yields than for triphenylsilane[367,622].

The introduction of chloroalkyl groups into organosilicon compounds sharply activates them in telomerisation with hexamethylcyclotrisiloxane[623]; the activity depends on the position of chlorine in the alkyl group relative to the silicon atom and decreases in the order: $\beta > \alpha > \gamma$.

Halogenoalkyl-substituted hydrido- and alkenyl-silanes can be used in additions. γ-Trifluoropropylalkenylchlorosilanes add to methylhydrochlorosilanes with the formation of

$$CF_3CH_2CH_2Si(Cl_2)(CH_2)_nSi(R)(CH_3)Cl$$

where R = Cl or CH_3 and $n = 2$ or 3.[624] Chloromethyldimethylsilane adds to

$$CH_2{=}CHCH(R)OSi(CH_3)_3$$

in the presence of Pt/C with the formation[488] of:

$$ClCH_2Si(CH_3)_2CH_2CH_2CH(R)OSi(CH_3)_3.$$

As the methyl groups in hexamethyldisiloxane are replaced by $\gamma\gamma\gamma$-trifluoropropyl groups the splitting of the siloxane bond by nucleophilic reagents is facilitated, but electrophilic reagents are hindered[586,587,625]. Silicon halides break the siloxane bond in $[R(CH_3)_2Si]_2O$, where R is $CF_3C(CH_3)_2$ or $Cl_2C_6H_3$, with formation of the corresponding halogenoalkyl(or aryl)dimethylhalogenosilanes[626].

Halogenoalkyl(or aryl)-containing organoacetoxysilanes undergo condensation with metal alkoxides. Compounds of the general formula $R_nR'_{3-n}SiOAl(OPr^{iso})_2$, where R = $CF_3CH_2CH_2$ or m-$CF_3C_6H_4$ and n = 1–3 have been obtained by the reaction of $R_nR'_{3-n}SiOCOCH_3$ with $Al(OPr^{iso})_3$.[627]

3. Reactions Accompanied by the Loss of a Halogen-Containing Group from Silicon

When aqueous NaOH acts on hexachlorocyclohexylmethyldichlorosilane the loss of $C_6H_6Cl_6$ is accompanied by dehydrochlorination and by the formation of 1,2,4-trichlorobenzene with 86.6% yield; hexachlorocyclohexylchloromethyldichlorosilane decomposes with the formation of chloromethane in addition to trichlorobenzene[184,186]. In the reaction of NaOH with chlorinated dimethyldichlorosilane and bis(trichloromethyl)diethoxysilane[18] the yields of $CHCl_3$ are 94.3 and 89.6% respectively. In 1-chloromethyl-1-methylsilacyclopentane the chloromethyl group is lost even on boiling with quinoline[512]; on boiling in the presence of water *sym*-dimethylbis(cyclotetramethylene)disiloxane is formed. In chloromethyl trichlorosilanes the mono- and di-chloro-substituted groups are completely stable even on boiling with anhydrous $FeCl_3$, and trichloromethyltrichlorosilane decomposes even in the absence of a catalyst with the formation of $SiCl_4$ and C_2H_4.[628]

In polyorganosiloxanes the stability of the halogenoalkyl groups is just the same as for the monomeric compounds, depends on the position of the halogen relative to the silicon atom. In $(CHF_2CF_2SiO_{1.5})_n$ and $(CHF_2CH_2SiO_{1.5})_n$ the Si–C bond is broken on shaking with 10% NaOH solution at 20°C; under these conditions $(CF_3CH_2CH_2SiO_{1.5})_n$ is completely stable[629].

The breaking of the Si–C bond also occurs with sodium, for example, on chloromethyltrimethylsilane[630] and also in the reaction of tetrakis(pentafluorophenyl)silane with lithium[385]:

$$(C_6F_5)_4Si + 2Li \rightarrow (C_6F_5)_3SiLi + C_6F_5Li\ .$$

The pentafluorophenyl group is lost under the action of bromine[385]:

$$(C_6F_5)_4Si + Br_2 \rightarrow (C_6F_5)_3SiBr + C_6H_5Br\ .$$

The presence of a halogenomethyl substituent greatly accelerates the solvolysis of organosilanes in alcohol–water medium[631,632], which here proceeds in two directions:

$$CH_2ClSi(CH_3)_2H + H_2O + OH^- \rightarrow CH_2ClSi(CH_3)_2OH + H_2 + OH^-\ , \quad (1)$$

$$CH_2ClSi(CH_3)_2H + H_2O + OH^- \rightarrow (CH_3)_3SiOH + H_2O + Cl^-\ . \quad (2)$$

The relative contribution of reaction (2) in this process depends on the nature of the halogenoalkyl radical and increases in the order: $CHCl_2 < CH_2Cl < CH_2I < CH_2Br$.

The hydrolysis of $(CH_3)_3SiSi(CH_3)_2CH_2Cl$ gives $[(CH_3)_3SiSi(CH_3)_2]_2O$.[49]

4. Physical Properties

There have been comparatively few studies of the physical properties of the halogenoalkyl(or aryl)-substituted organosilicon compounds.

The infrared[48,78,104,165,201,242,308,361,422,436,596,618,633–637], ultraviolet[253,635,638], Raman[49,267,350,637], electron absorption[281], NMR[77,78,120,140,201,253,308,639], nuclear quadrupole resonance[640–643], and proton magnetic resonance[644] spectra, polarographic behaviour[645], and electron microscopic examination of polyorganosiloxanes[646] have been described.

III. APPLICATIONS

Organosilicon compounds containing halogenated alkyl and aryl groups find application in various fields of technology[647,648].

For example, the use of organochlorosilanes with $\gamma\gamma\gamma$-trifluoropropyl[239] and α-(trichloromethyl)propyl[649] groups for the hydrophobisation of ceramic and other materials is known; halogenoalkyl-containing compounds are converted into nitro- and nitrito-derivatives for use in the pharmaceutical industry[446]. The replacement of alkyl and aryl groups in molecules of polyorganosiloxane liquids by halogenoalkyl and halogenoaryl groups markedly changes their properties, in particular, it increases the activation energy for viscous flow[634], increases chemical stability, and leads to a deterioration in their lubricating properties[650].

One of the most widely used types of liquid for these purposes are the $\gamma\gamma\gamma$-trifluoropropylmethylsiloxanes. They exhibit good lubricating properties on all metals[651]. In distinction from other organosilicon liquids polytrifluoropropylmethylsiloxanes are used successfully as lubricants for steel–steel couples[652].

Consistent lubricants based on these liquids[653,654] exhibit high stability to the action of water and solvents.

Liquids with other halogenoalkyl groups are used under the same designation, for example, $\alpha\alpha\gamma$-tribromopropyl, $\gamma\gamma\gamma$-trichloropropyl[316], β-(perfluoroalkyl)ethyl[655], ω-chloroalkyl[377], trifluorovinyl[419], and also bromophenyl[656], chlorophenyl[657], and chlorocyanoalkyl[92,658] groups. Liquid polyorganosiloxanes with molecules of formula p-$ClC_6H_4SCH_2CH_2Si(CH_3)O$ as elementary units of the chain exhibit good lubricating properties[331].

Linear polidimethylsiloxanes with $-[CH_2]_nCOOR$ terminal groups, where $R = CH_xF_{3-x}[CH_yF_{2-y}]_nCH_2-$ (x = 0–2, y = 0–2, n = 0–10),[659] $CHF_2[CF_2]_nCH_2-$ or $CClF_2.[CF_2CFCl]_nCH_2-$[660] are synthetic liquids which combine the best properties of organosilicon, fluorohydrocarbon, and ester oils. These liquids exhibit good viscosity characteristics over a wide range of temperatures, and a low freezing point; they are suitable for work under conditions of high temperature (205–260°C) and pressure. Analogous properties are exhibited by liquids with elementary unit of the chain molecule $OSi(CH_3)[CH_2]_4COOR$, where R = $C_3H_7CH_2$, $H[CF_2]_4CH_2$, or hexachlorobicycloheptenylmethyl[661].

Liquids which contain fluorinated organic groups are of great interest as dielectrics[239,644,662]. For example, a liquid of composition $[CF_3C_6H_4Si(CH_3)O]_n$ has ϵ = 6.5–9.5 in the range of temperatures from –20° to +100°C and frequencies of 100–100 000 Hz and is used as insulating impregnants of condensers.

Liquids containing hexafluoroisobutyl groups and active hydrogen are used for conferring oil-resistance on articles made of glass, metal, wood, leather, textiles, etc.[237]. Liquids with fluoroalkyl groups are used as fire-extinguishing materials[663], hydraulic liquids, and plasticisers[654].

Rubbers with β-(perfluoroalkyl)ethyl groups [664], in particular with trifluoropropylsiloxane units [238,654,665] and β-trifluoromethylpropyl [649] units are stable in air to 200°C and in a vacuum to 250°C. Polytrifluoropropylmethylsiloxane rubbers exhibit reduced residual deformation [666] and better technological properties [667] in comparison with polydimethylsiloxanes.

Unfilled arylenesiloxane vulcanisates with trifluoropropyl groups [663] have a tensile strength of 30 kgf cm^{-2} and when reinforced 90–105 kgf cm^{-2} at a relative elongation of 300–400%. Resins based on these rubbers retain their elasticity after radiation doses which considerably (more then 15 times) exceed that critical for polydimethylsiloxanes.

Rubbers with chloromethyl groups at silicon atoms are used [669,670]. The use of polyorganosiloxanes with halogenated alkyl groups in the composition with polytetrafluoroethylene is well known [671].

To obtain polymers with halogenophenyl groups, the method of catalytic polymerisation is widely employed. The introduction of halogenophenyl groups instead of phenyl groups greatly retards polymerisation [672,673]; depending on the number of chlorine atoms in the phenyl groups their effect on the retardation of the polymerisation process increases in the order [674]:

$$C_6H_5<ClC_6H_4<Cl_3C_6H_2<Cl_2C_6H_3<Cl_4C_6H.$$

The thermal stability of the polymers decreases with increase in the number of chlorine atoms in the phenyl group [675]. Polymers with halogenophenyl groups are used as non-inflammable adhesives for plastics, enamels, and glues in electrical insulating technology [676,677]. They also modify organic resins and lakes for conferring fire-resistance.

Polymers with halogenoalkyl ($CF_3CH_2CH_2$, [239] $Cl[CH_2]_n$, [377] $CHFClCF_2$, and $CHCl_2CCl_2$ [227]) and chlorocyanoalkyl [92] groups are used for obtaining plastics, decorative coatings, and other purposes.

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Institute of Organoelemental Compounds,
Academy of Science of the USSR, Moscow

Lenin All-Union Electrotechnical Institute, Moscow

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Progress in Organic Synthesis Based on 1-Alkoxydienes and 1-Alkoxypolyenes

S.M.Makin

This review covers the methods of preparation and chemical properties of 1-alkoxydienes and 1-alkoxypolyenes. The interest in 1-alkoxydienes arises because they form a basis for the easy production of various classes of organic compounds: aliphatic, carbocyclic, and heterocyclic. 1-Alkoxydienes have acquired the greatest importance in the synthesis of polyenes, including natural compounds of the vitamin A and β-carotene type. The higher cyanine dyes have become accessible on the basis of the 1-alkoxydienes.
The review deals with both theoretical and practical aspects of the chemistry of the 1-alkoxydienes and 1-alkoxypolyenes. The review surveys all the information available in world literature on the chemistry of the alkoxydienes and is intended for a wide circle of organic chemists, students, and research students. There is a bibliography of 86 references.

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I. INTRODUCTION

The extremely reactive 1-alkoxydienes, which possess a conjugated diene system and a labile alkoxy-group, are of great interest for synthetic organic chemistry. Studies in recent years have shown that these compounds can be used successfully to obtain aliphatic, carbocyclic, and heterocyclic compounds. However, 1-alkoxydienes are most frequently used for the synthesis of various types of unsaturated compounds, including polyenes belonging to the vitamin A series and carotenoids. The higher cyanines used as dyes also became accessible through the 1-alkoxydienes.

Progress in the field of synthesis and the use of 1-alkoxydienes has still not been surveyed in the chemical literature and the present review has the aim of filling this lacuna. Furthermore this review gives the information, still extremely scanty, about the 1-alkoxypolyenes.

II. SYNTHESIS OF 1-ALKOXY-1,3-DIENES

1. From Acetals of 3-Chlorobutyraldehyde

1-Alkoxy-1,3-dienes were first obtained by Wichterle[1] by heating dialkylacetals of 3-chlorobutyraldehyde with powdered potassium hydroxide; dehydrochlorination occurred with the simultaneous loss of alcohol:

$$CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2CH(OR)_2 \xrightarrow{KOH} CH_2=CH-CH=CHOR + ROH + HCl$$

where R = C_2H_5, n-C_3H_7, n-C_4H_9, iso-C_4H_9.

However, in this method of synthesis the yields of 1-alkoxydienes are very low (~10%) and poorly reproducible. Acetals of crotonaldehyde are usually formed exclusively instead of dienes[2]. Since alkoxydienes could not be obtained by this method in much later investigation[3] it must generally be taken as unsatisfactory.

2. From Ethynyl Vinyl Ethers

Shostakovskii and coworkers[4,5] proposed a method for obtaining 1-alkoxydienes by the partial hydrogenation of ethynyl vinyl ethers over a palladium catalyst. The initial ethers were obtained by the addition of alcohols to diacetylene:

$$CH\equiv C-C\equiv CH + ROH \rightarrow CH\equiv C-CH=CHOR \xrightarrow[Pd]{H_2} CH_2=CH-CH=CHOR,$$

where R = C_4H_9, C_6H_{11}, $C_{10}H_{17}$.

This method was also used for the synthesis of 4-substituted 1-alkoxydiene[6]:

$$C_3H_7-C\equiv C-CH=CHOC_2H_5 \xrightarrow[Pd]{H_2} C_3H_7CH=CH-CH=CHOC_2H_5.$$

3. From Vinylacetylene

Wichterle and Prochazka[7] obtained 1-ethoxybuta-1,3-diene by heating vinylacetylene and alcohol with alkali in an autoclave:

$$CH_2=CH-C\equiv CH + ROH \rightarrow CH_2=CH-CH=CH-OR.$$

According to Treibs[8,9], 1-alkoxybutadiene can be obtained by the addition of aliphatic or cycloaliphatic alcohols to vinylacetylene in the presence of alkali metal alkoxides.

In the production of diacetylene from 1,4-dichlorobutyne and potassium hydroxide solution in methanol Shostakovskii and Khomenko[10] observed the formation of a little 3-chloro-1-methoxybuta-1,3-diene together with other compounds:

$$ClCH_2-C\equiv C-CH_2Cl \rightarrow \left[CH_2=\underset{\displaystyle Cl}{\underset{|}{C}}-\underset{\displaystyle Cl}{\underset{|}{C}}=CH_2\right] \rightarrow CH_2=\underset{\displaystyle Cl}{\underset{|}{C}}-C\equiv CH \xrightarrow[KOH]{CH_3OH} CH_2=\underset{\displaystyle Cl}{\underset{|}{C}}-CH=CHOCH_3.$$

4. From Acetals of αβ-Unsaturated Aldehydes

Flaig[11] showed that 1-methoxy- and 1-ethoxy-butadiene are readily formed on passing the vapour of the corresponding acetals of crotonaldehyde over contact catalysts

such as NaH_2PO_4, $Al_2(SO_4)_3$, $MgSO_4$, or B_2O_3, at 300–350°C and reduced pressure.

In this way Nazarov and coworkers[12] succeeded in obtaining 1-methoxy- and 1-ethoxy-3-methylbutadiene from acetals of dimethylacrylaldehyde. 1-Butoxy- and 1-hexoxy-butadienes were obtained analogously[13] using Al_2O_3 as catalyst.

Nazarov and coworkers[14] developed a method for obtaining 1-alkoxydienes by the liquid-phase pyrolysis of acetals of $\alpha\beta$-unsaturated aldehydes, for example:

$$CH_3-\underset{\displaystyle R^1}{\underset{|}{C}}=CH-CH(OR)_2 \rightarrow CH_2=\underset{\displaystyle R^1}{\underset{|}{C}}-CH=CHOR,$$

where $R^1 = H$, CH_3.

This method consisted in heating acetals of $\alpha\beta$-unsaturated aldehydes at 165–220°C in the presence of catalysts of the acid type. The process goes in such a manner that the low-boiling alcohols and 1-alkoxydiene formed during the pyrolysis are continuously removed from the reaction zone.

5. From Acetals of Vinylacetaldehyde

A convenient method for obtaining 1-alkoxybutadienes is the pyrolysis of acetals of vinylacetaldehyde[15,16], which can be obtained readily by the condensation of alkyl vinyl ethers in the presence of the complex catalysts $BF_3.O(C_2H_5)_2$ + $Hg(OCOCH_3)_2$ or $BF_3.O(C_2H_5)_2$ + HgO:[15,17]

$$2CH_2=CHOR \xrightarrow[Hg(OCOCH_3)_2]{BF_3\cdot O(C_2H_5)_2} CH_2=CH-CH_2CH(OR)_2 \rightarrow CH_2=CH-CH=CHOR,$$

where R = C_2H_5, n-C_4H_9, iso-C_5H_{11}.

The alcohol is removed at 330–350°C in the presence of the catalysts $MgHPO_4.Na_2SiO_3$ [15] or $BaO.SiO_2$,[16] the yield of the dienes being > 70%.

6. From 1,1,3-Trialkoxyalkanes

The most general and convenient method for obtaining 1-alkoxydienes is the pyrolysis of 1,1,3-trialkoxyalkanes:

$$R^1CH_2-\underset{\displaystyle OR}{\underset{|}{CR^2}}-CHR^3-CH(OR)_2 \rightarrow \underset{\displaystyle R^1}{\underset{|}{CH}}=\underset{\displaystyle R^2}{\underset{|}{C}}-\underset{\displaystyle R^3}{\underset{|}{C}}=CHOR + 2ROH.$$

This method allows 1-alkoxydienes with various substituents, both in the diene part and in the alkoxy-residue, to be synthesised in high yield[11,12,14,18–24] (see Table 1).

The initial 1,1,3-trialkoxyalkanes are readily obtained by the condensation of acetals and ketals with alkyl vinyl ethers in the presence of aprotic acids[25,26]:

$$R^1CH_2-CR^2(OR)_2 + R^3-CH=CHOR \xrightarrow{BF_3\cdot O(C_2H_5)_2} R^1CH_2-\underset{\displaystyle OR}{\underset{|}{CR^2}}-CHR^3-CH(OR)_2.$$

This method of synthesis of the 1,1,3-trialkoxyalkanes acquired real practical importance in connection with the development of a practicable method of obtaining ketals and acetals with the aid of tetra-alkoxysilanes[28]. Of the other methods of synthesis of the initial compounds mention must be made of a convenient way of obtaining 1,1,3-trialkoxybutanes from crotonaldehyde and an alcohol[17]:

$$CH_3CH=CH-CHO + ROH \xrightarrow{HCl} CH_3-\underset{\displaystyle OR}{\underset{|}{CH}}-CH_2-CH(OR)_2.$$

The exchange of the alkoxy-groups of 1,1,3-trimethoxy- and 1,1,3-triethoxy-alkanes with higher alcohols allows trialkoxy-compounds with other alkoxy-residues to be obtained easily. Such trialkoxy-derivatives are the starting substances for the synthesis of 1-alkoxydienes with heavy alkoxy-groups[27]:

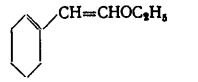
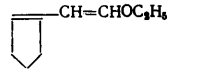
$$CH_3CR^1(OR)-CHR^2-CH(OR)_2 \xrightarrow[-2ROH]{+2R^1OH} CH_3CR^1(OR^1)-CHR^2-CH(OR^1)_2.$$

The production of 1-alkoxydienes by the pyrolysis of 1,1,3-trialkoxyalkanes is carried out in two ways: vapour-phase and liquid-phase.

In the vapour-phase method for the production of 1-alkoxydienes the vapour of trialkoxyalkanes is passed at reduced pressure over a catalyst at 300–350°C. The catalysts which are used include: $BaO.4SiO_2$ or $BaO.5SiO_2$; $Al_2(SO_4)_3$, $MgSO_4$, NaH_2PO_4, B_2O_3, SiO_2, $MgHPO_4$, and $AlPO_4$.[11,12,14,15,22,27]

It has been shown[12,14,22,29] that the best yields of 1-alkoxydienes are obtained by using $MgHPO_4$ and this catalyst lasts longest.

Table 1. Yields of 1-alkoxydienes in the pyrolysis of 1,1,3-trialkoxyalkanes.

1-Alkoxydiene	Yield, %		Reference
	vapour-phase process	liquid-phase process	
$CH_2=CH-CH=CHOCH_3$	64.0	—	11,12
$CH_2=CH-CH=CHOC_2H_5$	72.0	77.5	11,12,13
$CH_2=CH-CH=CHOC_4H_9$-n	42.0	—	27
$CH_2=CH-CH=CHOC_5H_{11}$-iso	37.0	—	27
$CH_2=CH-CH=CHOC_6H_{13}$-n	43.0	—	27
$CH_3CH=CH-CH=CHOC_2H_5$	71.5	65.0	14,24
$CH_2=C(CH_3)-CH=CH-OCH_3$	71.0	—	12
$CH_2=C(CH_3)-CH=CH-OC_2H_5$	77.0	64.0	12,14,23–24
$CH_2=C(CH_3)-CH=CH-OC_4H_9$-n	51.5	52.0	14,27
$CH_2=C(CH_3)-CH=CH-OC_5H_{11}$-iso	—	43.5	27
$CH_2=CH-(CH_3)C=CHOC_2H_5$	62.0	68.3	14,24
$CH_2=CH-(CH_3)C=CHOC_5H_{11}$-iso	41.0	—	27
$C_2H_5CH=CH-CH=CHOC_2H_5$	—	68.6	14
$(CH_3)_2C=CH-CH=CHOC_2H_5$	—	77.8	14
$CH_2=C(CH_3)-C(CH_3)=CHOC_2H_5$	—	65.0	14,24
$CH_3-CH=CH-C(CH_3)=CHOC_2H_5$	—	59.0	14,24
	75.4	82.0	14
	—	83.2	14

The liquid-phase pyrolysis of 1,1,3-trialkoxyalkanes is carried out just as for the acetals of $\alpha\beta$-unsaturated aldehydes (see above). NaH_2PO_4, $NH_4H_2PO_4$, *p*-toluenesulphonic acid[29], and *p*-toluenesulphonic acid–quinoline mixture[23,24] have been used as catalysts[14,21], the best being $NH_4H_2PO_4$ and *p*-$CH_3C_6H_4SO_3H$–quinoline.

It should be noted that when a mixture of *p*-toluenesulphonic acid and quinoline is used as catalyst the pyrolysis of alkoxyalkanes with a terminal isoprenyl group $CH_2=C(CH_3)-$, rearrangement is observed, with the formation of 1-alkoxydienes with an n-propenyl structure $CH_3-CH=CH-$, the content of which in the reaction products reaches 10–20%:[30]

$$CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-\underset{\displaystyle R}{\underset{|}{C}}=CH-OC_2H_5 \rightarrow CH_3CH=CH-\underset{\displaystyle R}{\underset{|}{C}}=CHOC_2H_5$$

where R = H, CH_3.

7. From Phosphonates of γ-Vinyl Ethers and Carbonyl Compounds (According to Khorner)

In this method the phosphonates of γ-vinyl ethers, which can be obtained by the pyrolysis of the acetals of γ-carbonylphosphonates, react with carbonyl compounds in the presence of a base (sodium hydride) in a medium of hexamethylphosphotriamide[31]. As a result 1-alkoxydienes are formed:

$$(RO)_2\overset{\displaystyle O}{\underset{|}{P}}-CH_2CH_2-\underset{\displaystyle R^1}{\underset{|}{C}}(OC_2H_5)_2 \rightarrow (RO)_2\overset{\displaystyle O}{\underset{|}{P}}-CH_2-CH=\underset{\displaystyle R^1}{\underset{|}{C}}-OC_2H_5$$

$$\xrightarrow{O=CR^2R^3} R^2R^3C=CH-CH=CR^1-OC_2H_5.$$

This method is extremely laborious and the initial compounds are not readily available; however, it allowed 1-ethoxydienes with structures which could not be made by other methods to be obtained. Table 2 gives the yields of the 1-ethoxydienes obtained by this method[31].

Table 2. Yields of 1-alkoxydienes after Sturtz and Lavielle[31].

Ethoxydiene	Yield %	Ethoxydiene	Yield %
$(C_6H_5)_2C{=}CH{-}CH{=}CHOC_2H_5$	68	cyclo-$C_6H_{10}{=}CH{-}CH{=}CHOC_2H_5$	37
$C_6H_5CH{=}CH{-}CH{=}CHOC_2H_5$	48	$(C_6H_5)_2C{=}CH{-}CH{=}C(CH_3){-}OC_2H_5$	40
p-$CH_3OC_6H_4{-}CH{=}CH{-}CH{=}CHOC_2H_5$	47	p-$CH_3OC_6H_4CH{=}CHCH{=}C{-}OC_2H_5$	40
p-$(CH_3)_2NC_6H_4CH{=}CH{-}CH{=}CHOC_2H_5$	48	CH_3	
$(CH_3)_2CH{-}CH{=}CH{-}CH{=}CHOC_2H_5$	57		
$C_2H_5{-}C(CH_3){=}CH{-}CH{=}CHOC_2H_5$	33	cyclo-$C_6H_{10}{=}CH{-}CH{=}C(CH_3){-}OC_2H_5$	40

8. Geometrical Isomerism of 1-Alkoxydienes

The problem of the geometric isomerism of 1-alkoxydienes has been repeatedly mentioned in the literature but a conclusive solution has not yet been obtained.

In 1950 Farmilo and Nichols[20] reported that in the pyrolysis of 1,1,3-trimethoxybutane isomeric *cis*- and *trans*-1-methoxybutadienes are formed, the proportion of the *cis*-isomer being ~ 60%. Their conclusion that *cis*–*trans* isomerism existed in the reaction products was based on the fact that in the reaction with maleic anhydride an addition product corresponding to the *trans*-isomer is readily formed, whereas under these conditions the *cis*-isomer evidently does not give an adduct with maleic anhydride, but polymerises.

In 1964 Štěpek[32] studied the problem of the existence of geometric isomers of 1-methoxybutadiene, but despite extreme care could not isolate *cis*- and *trans*-isomers. On the other hand, kinetic investigations of the reaction of 1-methoxybutadiene with maleic anhydride showed that this reaction actually proceeds in two directions—diene synthesis and copolymerisation—however, this is explained not by the existence of stable *cis*- and *trans*-isomers, as has been suggested[20], but signifies that two parallel reactions with different mechanisms occur. Copolymerisation proceeds by a radical mechanism, whereas the diene addition is not affected by either radical initiators or inhibitors. In this connection Štěpek assumes that Farmilo and Nichols[20] erroneously took to be the *cis*-isomer of 1-methoxybutadiene a certain amount of the dimethylacetal of crotonaldehyde, which is obtained in the synthesis of 1-methoxybutadiene.

In 1967 it was shown[33], with the aid of infrared spectroscopy and gas-liquid chromatography that the 1-methoxybutadiene obtained by the loss of alcohol from 1,1,3-trimethoxybutane in the presence of phosphoric acid as catalyst[34] is the pure *trans*-isomer.

However, Martin and coworkers[35], who employed semi-preparative gas–liquid chromatography succeeded in isolating small quantities of a strongly enriched mixture and in some instances, the pure *cis*- and *trans*-isomers of 1-ethoxy-1,3-dienes

$$R{-}CH{=}C(R^1){-}C(R^2){=}CHOC_2H_5,$$

(where R, R^1, and R^2 = H, CH_3) and of identifying them by the NMR method. Furthermore, the NMR method was used to study the relative stability of compounds unsubstituted at the end of the chain (R = H) and to determine the equilibrium constants of the *cis*–*trans* isomerisation. On the basis of the results obtained it was concluded that the *trans*-1,2-isomer is always more stable than the *cis*-1,2-isomer and substitution at the double bond increases the stability of the *cis*-1,2-configuration.

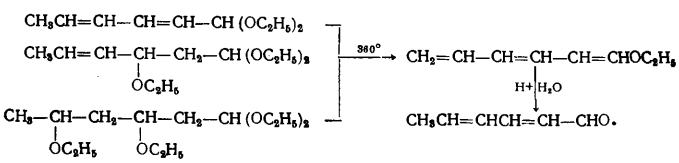
The ultraviolet and infrared spectra of the 1-alkoxydienes, both unsubstituted and with various substituents in the chain, have been investigated[27]. All the 1-alkoxydienes have an absorption band in the 235–247 nm range (in heptane), displaced considerably to longer wavelengths in comparison with the absorption band of butadiene (~ 217 nm [36]).

In the infrared spectra the frequency of the stretching vibrations of the C–C bond of the 1-alkoxydienes lies in the same range as for the alkyl derivatives of butadiene (~ 1650 cm^{-1}); splitting of the lines of the C–C bond is sometimes observed.

III. SYNTHESIS OF 1-ALKOXYPOLYENES

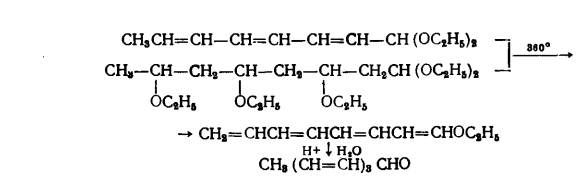
1-Alkoxypolyenes, like 1-alkoxydienes, are vinylogues of the simple vinyl ethers. Makin and Sudakova[37] showed that the pyrolysis of acetals and alkoxyacetals is universal and can be used with success not only for the synthesis of simple vinyl and diene ethers but also for the synthesis of 1-alkoxypolyenes.

In the vapour-phase pyrolysis of the acetal of 2,4-hexadienaldehyde and also of 1,1,3-triethoxyhex-4-ene over $MgHPO_4$, Na_2SiO_3 as catalyst at 360°C and reduced pressure, 1-ethoxyhexa-1,3,5-triene is formed in > 70% yield:



The structure of 1-ethoxyhexa-1,3,5-triene was confirmed by the presence in the ultraviolet spectrum of an absorption maximum at 272 nm (in heptane), which is characteristic for three conjugated bonds. In the hydrolysis of 1-ethoxyhexatriene by a dilute solution of sulphuric acid, hexa-2,4-dienaldehyde is formed. 1-Ethoxyhexa-1,3,5-triene is readily polymerised in air but in nitrogen at 0°C it can be kept for several months.

Similarly, 1-ethoxyocta-1,3,5,7-tetraene was obtained in 49–54% yield by the pyrolysis of either octatrienal acetal or 1,1,3,5,7-pentaethoxyoctane over acid phosphates[37]:



1-Ethoxytetraene is unstable and is converted into octa-2,4,6-trienal on hydrolysis in acid.

IV. SYNTHESIS ON THE BASIS OF 1-ALKOXY-1,3-DIENES

1. Hydrogenation

The exhaustive hydrogenation of 1-alkoxydienes in the presence of platinum black, $Pd/CaCO_3$, or nickel catalysts leads to ethers[33,38]. Thus butyl methyl, ethyl isopentyl, and butyl isopentyl ethers were obtained from 1-methoxybuta-1,3-diene, 1-ethoxy-3-methylbuta-1,3-diene, and 1-butoxy-3-methylbuta-1,3-diene respectively. The partial hydrogenation of 1-alkoxydienes does not take place selectively, but with the formation of a mixture of isomeric compounds[33,39], as is shown in the scheme. The addition of 1 mole hydrogen to *trans*-1-methoxybuta-1,3-diene gives a mixture of all possible hydrogenation products[33]:

$$CH_2{=}CHCH{=}CHOCH_3 + H_2 \rightarrow \underset{\text{1,2- addition}}{CH_2{=}CHCH_2CH_2OCH_3} +$$
$$+ \underset{\text{1,4- addition}}{CH_3CH{=}CHCH_2OCH_3} + \underset{\text{3,4- addition}}{CH_3CH_2CH{=}CHOCH_3} + \underset{\text{complete hydrogenation}}{C_4H_9OCH_3}$$
cis- and *trans*- *cis* and *trans*-

In the presence of platinum black and especially palladium catalyst the main product is *trans*-1-methoxybut-1-ene (3,4-addition). Partial hydrogenation in the presence of Raney nickel catalyst gives almost equal amounts of the products of 1,2-, 3,4-, and 1,4-addition.

2. Hydrolysis

The hydrolysis of 1-alkoxydienes under the action of 2% sulphuric acid leads $\alpha\beta$-unsaturated aldehydes[38]:

$$R{-}CH{=}\overset{R^1}{\overset{|}{C}}{-}CH{=}CHOC_2H_5 \xrightarrow[H^+]{H_2O} RCH_2{-}\overset{R^1}{\overset{|}{C}}{=}CH{-}CHO$$

where R, R^1 = H, CH_3.

In this way crotonaldehyde, 3-methylcrotonaldehyde, and 4-methylcrotonaldehyde were obtained in good yield from 1-ethoxybuta-1,3-diene, 1-ethoxy-3-methylbuta-1,3-diene, and 1-ethoxypenta-1,3-diene respectively. Probably the addition of water to 1-alkoxydienes occurs in the 1,4-position of the diene system, although it is difficult to draw definite conclusions since $\beta\gamma$-unsaturated aldehydes (obtained when there is 1,2-addition) readily rearrange in acid medium into $\alpha\beta$-unsaturated aldehydes.

3. Addition of [Substituted] Silanes

It was shown recently that 1-alkoxydienes are capable of adding silane derivatives[40]. The addition of fluoromethylpropylsilanes to a diene ether takes place in the presence of hydrogen hexachloroplatinate(IV) with the formation of 1-butoxy-4-(fluoromethylpropylsilyl)but-1-ene with yields of up to 91%; an addition product with two molecules of the silane is liberated in small amounts:

$$C_4H_9OCH{=}CH{-}CH{=}CH_2 + HSiRR'F \begin{cases} \rightarrow C_4H_9OCH{=}CHCH_2CH_2SiRR'F \\ \rightarrow C_4H_9OCH_2CH(SiRR'F){-}CH_2CH_2SiRR'F. \end{cases}$$

Here we encounter a rare instance of addition to 1-alkoxydienes in the 1,2- and 3,4-positions.

The reaction of methyldichlorosilane with 1-butoxybuta-1,3-diene is accompanied by resinification of the ether and the addition product could be isolated only in 1.2% yield.

4. Addition of Alchols

1-Alkoxy-1,3-dienes add alcohols even in the cold or at room temperature in the presence of catalytic amounts of hydrochloric acid, acetals of $\alpha\beta$-unsaturated aldehydes being obtained in good yield[14,38,41]:

$$CH_2{=}\overset{R^1}{\overset{|}{C}}{-}CH{=}CHOR + ROH \xrightarrow{H^+} CH_2{=}\overset{R^1}{\overset{|}{C}}{-}CH{-}CH(OR)_2$$

where R^1 = H, CH_3; R = CH_3, C_2H_5, n-C_4H_9, iso-C_5H_{11}.

The structure of the reaction products was shown by countersyntheses and infrared spectroscopy[38].

The diethyl-, dibutyl-, and di-isopentyl-acetals of crotonaldehyde were obtained in this way from 1-ethoxy-, 1-butoxy-, and 1-isopentyloxy-butadiene respectively[38,41] and the diethyl- and dibutyl-acetals of 3-methylcrotonaldehyde were obtained from ethoxy- and butoxy-isoprene[14,38].

Kubler[42], having studied the addition of methanol to 1-methoxybutadiene and of ethanol to 1-ethoxybutadiene in the presence of sulphuric acid, states that this reaction is accompanied by the formation of 1,1,5-trialkoxyocta-2,6-dienes by the scheme:

$$CH_2{=}CH{-}CH{=}CHOCH_3 + H^+ \rightarrow CH_3CH{=}CH{-}\overset{+}{C}HOCH_3 \rightarrow$$
$$\xrightarrow{CH_2=CH-CH=CHOCH_3} CH_3CH{=}CHCH(OCH_3)CH_2CH{=}\overset{+}{C}HOCH_3 \rightarrow$$
$$\xrightarrow{CH_3OH} CH_3CH{=}CH{-}CH(OCH_3)CH_2CH{=}CHCH(OCH_3)_2 + H^+.$$

It should be noted that the addition of alcohols to 1-alkoxydienes can serve as a preparative method for obtaining difficultly accessible acetals from $\alpha\beta$-unsaturated aldehydes.

5. Bromination and Bromoalkoxylation

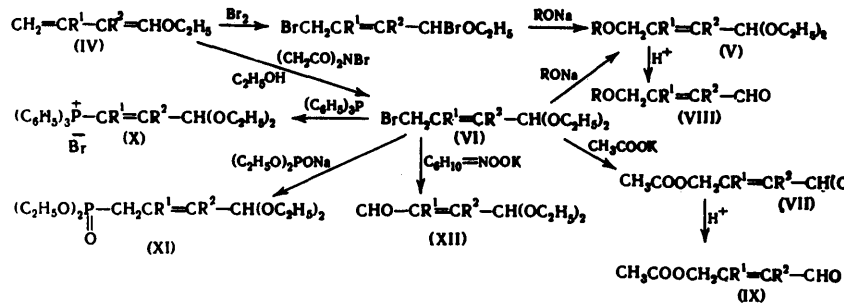
1-Ethoxybutadiene adds the first bromine molecule in the 1,4-position of the diene system. In further bromination a second bromine molecule is added with the formation of a crystalline tetrabromide[11]:

$$CH_2{=}CH{-}CH{=}CHOC_2H_5 \xrightarrow{Br_2} CH_2{-}\underset{Br}{CH}{=}CH{-}\underset{Br}{CHOC_2H_5} \xrightarrow{Br_2}$$
$$\rightarrow \underset{(I)}{CH_2{-}\underset{Br}{CH}{-}\underset{Br}{CH}{-}CHOC_2H_5}.$$
$$\underset{Br\ \ Br\ \ Br\ \ Br}{\ }$$

Both the dibromide (I) and, in particular, the tetrabromide are very unstable compounds. On treating dibromide (I) with sodium ethoxide it is converted into an acetal of 4-ethoxycrotonaldehyde (II) and the loss of alcohol from (II) yielded 1,4-diethoxybuta-1,3-diene (III):[11]

$$(I) \xrightarrow{2C_2H_5ONa} \underset{(II)}{C_2H_5OCH_2CH{=}CHCH(OC_2H_5)_2} \xrightarrow[Al_2O_3]{350^\circ} \underset{(III)}{C_2H_5OCH{=}CHCH{=}CHOC_2H_5}.$$

The bromination of substituted 1-alkoxydienes (IV) has been studied[38], and the direction of the reaction and structure of the bromides obtained was established from the products of their reaction with alkoxides. The formation of acetals of $\alpha\beta$-unsaturated γ-alkoxyaldehydes (V) shows that the addition of bromine occurs in the 1,4-position.



where R = CH_3, C_2H_5; R^1 and R^2 = H, CH_3.

The bromoalkoxylation of 1-alkoxydienes (IV) is extremely interesting and promising. This reaction, which takes place on the treatment of 1-alkoxydienes with bromosuccinimide in alcoholic medium leads to acetals of $\alpha\beta$-unsaturated 4-bromoaldehydes (VI).[11,38] Using the high reactivity of allyl bromide, various difficultly accessible bifunctional derivatives of $\alpha\beta$-unsaturated aldehydes[38] were readily obtained, a route of wide use in organic synthesis. The bromoalkoxylation of 1-ethoxybuta-1,3-diene[11,38], 1-ethoxy-2-methylbuta-1,3-diene[38], and 1-ethoxy-3-methylbuta-1,3-diene[38] was investigated.

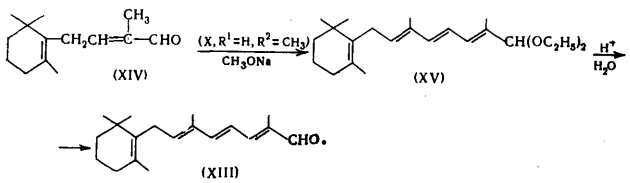
The reaction of 4-bromoacetals (VI) with alkoxides or potassium acetate gave in good yield the acetals of γ-alkoxy- (V) and γ-acetoxy- (VII) derivatives of $\alpha\beta$-unsaturated aldehydes respectively. In the hydrolysis by dilute phosphoric acid, (V) and (VII) are readily converted into the corresponding γ-alkoxy- (VIII) and γ-acetoxy- (IX) substituted $\alpha\beta$-unsaturated aldehydes[38].

γ-Bromoacetals (VI) react readily with triphenylphosphine with the formation of phosphonium salts[29,43-45] (X), and on reaction with sodium diethyl phosphite they are converted into phosphonates (XI).[29]

The bromomethyl group in 4-bromoacetals (VI) can be oxidised to an aldehyde group by reaction with the potassium salt of nitrocyclohexane[38,46,47]. This provides a possible route to the previously difficultly accessible monoacetals of fumaraldehyde and its alkylsubstituted derivatives (XII).

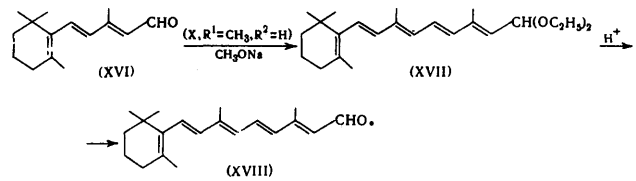
The bifunctional derivatives of $\alpha\beta$-unsaturated aldehydes obtained on the basis of 1-alkoxydienes were used for the synthesis of polyene compounds of various types and principally for the synthesis of derivatives of vitamin A and carotenoid precursors.

Thus, 1-ethoxy-2-methylbutadiene was used for obtaining β-C_{19}-aldehyde (XIII)[44], which is a key product in the synthesis of β-carotene:

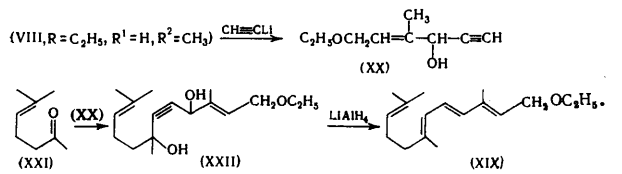


Here the reaction of the phosphonium salt (X; R^1 = H, R^2 = CH_3) with β-C_{14} aldehyde (XIV) in the presence of sodium methoxide gave an acetal of β-C_{19} aldehyde (XV), hydrolysis of which by dilute phosphoric acid gave quantitatively a mixture of the *cis–trans*-isomers of β-C_{19} aldehyde (XIII).

Similarly, reaction of β-ionolydeneacetaldehyde (XVI) with a phosphonium salt (X; R^1 = CH_3, R^2 = H) obtained from 1-ethoxy-3-methylbutadiene, gave the acetal of the aldehyde of vitamin A (XVII), which forms on acid hydrolysis the aldehyde of vitamin A (XVIII)[45]:

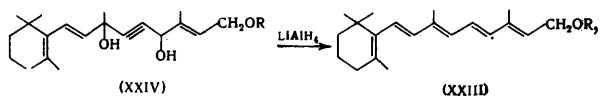


Several synthetic routes to the polyene ethers of isoprenoid structure (including ethers of vitamin A) have been proposed on the basis of 1-alkoxydienes. The scheme given below shows the synthesis of the ethyl ether of dehydrofarnesol (XIX)[48]:



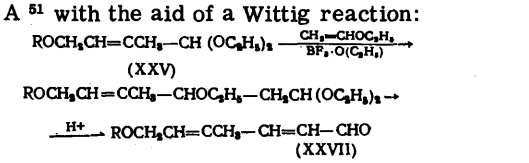
In this synthesis the condensation of 1-ethoxy-3-methylhex-2-en-5-yn-4-ol (XX) with methylheptenone (XXI) gave the acetylenic glycol (XXII), which on reaction with lithium tetrahydroaluminate was converted into the ethyl ether of dehydrofarnesol (XIX) (the Nayler–Whiting reaction[49]).

This reaction was subsequently used to obtain the ethyl ether of vitamin A (XXIII):[50]



where R = C_2H_5. The initial acetylenic glycol (XXIV) was obtained by two paths: (1) by condensation of β-ionone with the Iotsich complex obtained from (XX), and (2) from ethynyl-β-ionol and γ-ethoxytiglinaldehyde (VIII; R = C_2H_5, R^1 = H, R^2 = CH_3).

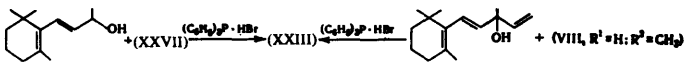
γ-Alkoxy- and γ-acetoxy-tiglinaldehydes and their acetals obtained from the corresponding 1-alkoxydienes open yet another synthetic route to the esters and ethers of vitamin A[51] with the aid of a Wittig reaction:



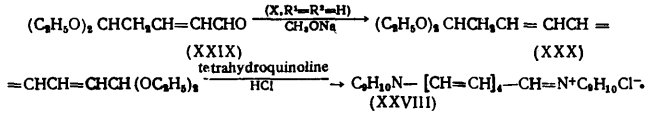
where R = CH_3, $COCH_3$.

The acetals of γ-methoxy- and γ-acetoxytiglinaldehyde (XXV) readily condense with ethyl vinyl ether with the formation of the corresponding 1,1,3-trialkoxy-compounds (XXVI), which on heating with acetic acid are converted

into ω-substituted hexadienals (XXVII). Ethers of vitamin A (XXIII; R = CH_3, $COCH_3$) were synthesised[51] subsequently, as is shown by the scheme:



The reactions of 1-alkoxydienes considered above can be used successfully for the synthesis of cyanines. Thus the acetal of γ-bromocrotonaldehyde, obtained from 1-ethoxybutadiene, was used for making the cyanine (XXVIII)—an intermediate in the synthesis of pentacarbocyanine sensitisers[29,52]:

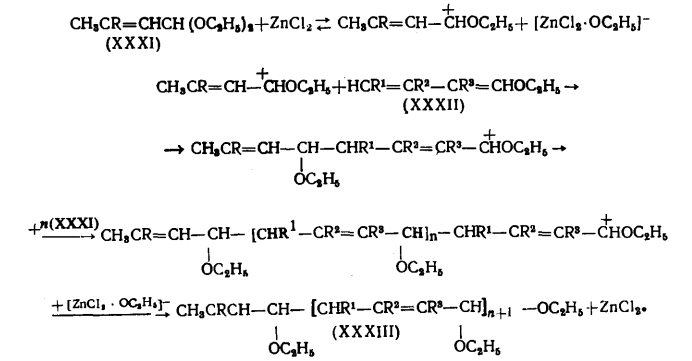


Here the condensation of 5,5-diethoxypent-2-enal[52,53] (XXIX) with 4-(1,1-diethoxybut-2-enyl)triphenylphosphonium bromide (X; $R^1 = R^2 = H$) in the presence of sodium methoxide gives nonatriendial tetraethyl acetal (XXX), which on treatment with tetrahydroquinoline in hydrochloric acid is readily converted into (XXVIII).

6. Condensation with Acetals of $\alpha\beta$-Unsaturated Aldehydes

Nazarov and Krasnaya showed[54,55] that 1-alkoxydienes, like alkyl vinyl ethers, readily condense with the acetals of $\alpha\beta$-unsaturated aldehydes in the presence of aprotic acids —$ZnCl_2$, $BF_3.O(C_2H_5)_2$, etc. For example, it was shown that in the condensation of the acetals of crotonaldehyde and β-methylcrotonaldehyde with 1-ethoxybuta-1,3-diene, 1-ethoxy-3-methylbuta-1,3-diene[54,55], 1-ethoxy-2-methylbuta-1,3-diene[56], 1-ethoxypenta-1,3-diene[57], and 1-ethoxy-2,3-dimethylbuta-1,3-diene[56], the addition of acetals to 1-alkoxydienes, whether substituted or unsubstituted, takes place in the 1,4-position of the diene system of the 1-alkoxydiene.

The addition of acetals (XXXI) to 1-alkoxydienes (XXXII) yields new acetals of $\alpha\beta$-unsaturated aldehydes, which in their turn are also capable of addition to 1-alkoxydienes so that a mixture of the first, second, third, and other successive addition products (XXXIII) is obtained, readily separable by fractional distillation. The mechanism of this condensation is as follows[56]:



Hence the addition of acetals to 1-alkoxydienes has the character of telomerisation, the extent of which depends on the ratio of the acetal and alkoxydiene taken in the reaction.

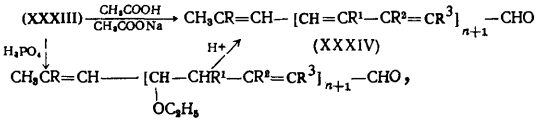
The example of the condensation of crotonaldehyde acetal with 1-ethoxypenta-1,3-diene was used[57] to investigate the dependence of the composition of the telomeric products on the ratio of the acetal to 1-alkoxydiene; the results are given in Table 3.

Table 3 shows that a change in the alkoxydiene : acetal ratio allows the course of the reaction to be regulated to some extent, by directing it to the side of the preferential formation of the desired product. A similar picture is also observed for other 1-alkoxydienes and acetals. The reaction examined is a comparatively simple method of growing a chain of 4, 8, 12, or 16 carbon atoms at one stroke.

Table 3. Telomerisation[57] of acetals of crotonaldehyde with 1-ethoxypenta-1,3-dienes.

Alkoxydiene : acetal ratio	Yield of telomer (XXXIII $R' = CH_3$, $R = R^2 = R^3 = H$)				
	$n=0$	$n=1$	$n=2$	$n=3$	total
1:2	48	30	12	3	93
2:3	28	41	16.5	5	90.5
1:1	27	12	37	8.5	84.5
2:1	9.5	6	26	26.5	68

A remarkable property of alkoxyacetals (XXXIII) was that on heating with 90% acetic acid they are converted in high yield into polyene aldehydes (XXXIV) and on heating with dilute phosphoric acid are hydrolysed with quantitative formation of alkoxyaldehydes (XXXV) which under the action of *p*-toluenesulphonic acid in toluene are also readily converted into polyenals (XXXIV)[54-57].

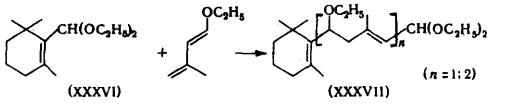


where R, R^1, R^2, R^3 = H, CH_3; n = 0, 1, 2.

The condensation of acetals of $\alpha\beta$-unsaturated aldehydes with 1-alkoxydienes has made the natural polyenes of the isoprenoid structure extremely accessible.

The conversions considered above were used for the synthesis of β-ionolideneacetaldehyde, the aldehyde of vitamin A, and vitamin A (alcohol).

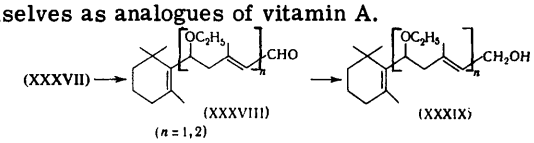
The condensation of β-cyclocitral acetal (XXXVI) with 1-ethoxyisoprene in the presence of zinc chloride as catalyst yielded[58] a mixture of the ethoxyacetals of C_{15} aldehyde (XXXVII; n = 1) and the C_{20} aldehyde (XXXVII; n = 2) with yields of 44.6 and 25% respectively:



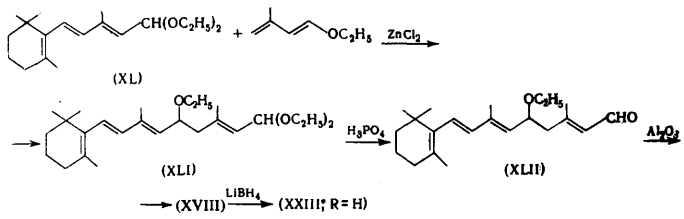
Under the action of orthophosphoric acid in dioxan, (XXXVII; n = 1) is converted into β-ionolideneacetaldehyde (XVI) and on hydrolysis with dilute phosphoric acid,

into ethoxydihydro-β-ionolideneacetaldehyde (XXXVIII, $n = 1$) in good yield. Reduction of (XXXVIII; $n = 1$) with sodium tetrahydroborate gives ethoxydihydro-β-ionolideneethanol (XXXIX; $n = 1$).

In a similar manner, the diethoxybisdihydroaldehyde of vitamin A (XXXVIII; $n = 2$) and diethoxybisdihydrovitamin A (XXXIX; $n = 2$) were obtained in good yield from (XXXVII; $n = 2$). These compounds can be used for the synthesis of vitamin A and in addition they are of interest themselves as analogues of vitamin A.

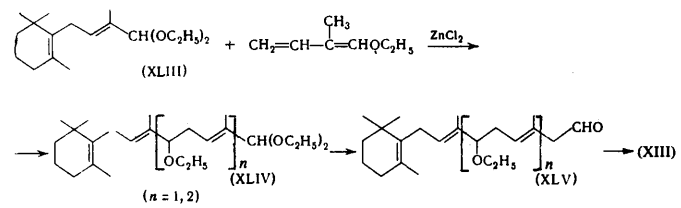


Vitamin A was synthesised by the condensation of β-ionolideneacetaldehyde (XL) with 1-ethoxyisoprene [59,60]. The ethoxyacetal (XLI) thus obtained in 62% yield hydrolyses quantitatively into dihydrovitamin A ethoxyaldehyde (XLII), which on chromatography on aluminium oxide gives the vitamin A aldehyde (XVIII):



On reduction of (XVIII) with lithium tetrahydroborate vitamin A (XXIII, R = H) is obtained.

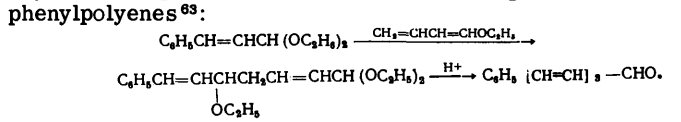
The method described above for growing a polyene chain was used for the synthesis of β-C_{19} aldehyde (XIII) [61].



With this aim the β-C_{19} ethoxyacetal (XLIV; $n = 1$) and β-C_{24}-diethoxyacetal (XLIV; $n = 2$) were obtained by the addition of β-C_{14} aldehyde acetal to 1-ethoxy-2-methylbutadiene. The hydrolysis of these ethoxyacetals with dilute phosphoric acid gives, in quantitative yield, β-C_{19}-ethoxyaldehyde (XLV; $n = 1$) and β-C_{24}-diethoxyaldehyde (XLV; $n = 2$) respectively. Removal of alcohol from (XLV; $n = 1$) led to the fully *trans*-β-C_{19}-aldehyde (XIII).

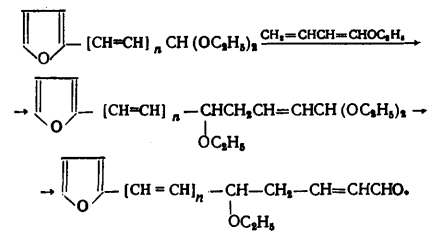
It has been shown [62] that citral acetal is also capable of being condensed with 1-ethoxyisoprene, to form a mixture of telomers of isoprenoid structure.

The condensation of cinnamaldehyde acetal with 1-ethoxybutadiene provided a new method for the production of phenylpolyenes [63]:



In this way the acetals of αβ-unsaturated aldehydes are readily condensed with 1-alkoxydienes. However, there is almost no information about a similar condensation for ketals. The reaction of acetophenone ketal with 1-ethoxybutadiene has been described [64], it being noted that the yield of the condensation product was very low.

Furfural acetal and β-(2-furyl)acrolein acetal readily add to 1-ethoxybutadiene to form normal condensation products [63]:

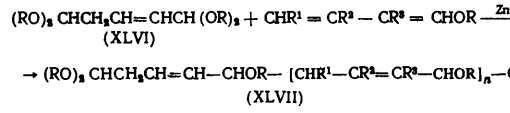


($n = 0$ or 1; yield 40%).

The condensation of 1-alkoxydienes with diacetals of glutaconaldehyde (XLVI) is very interesting, since it allowed previously inaccessible cyanines—the derivatives of higher polyene dialdehydes—to be synthesised simply [29,65-67].

Glutaconaldehyde acetals have two acetal groups, one of which is αβ-unsaturated, the other βγ-unsaturated. It was found experimentally that the condensation of glutaconaldehyde acetal takes place selectively, solely at the αβ-unsaturated acetal group, and the βγ-unsaturated group does not participate in the reaction. This course for the reaction agrees with the theoretical ideas about the mechanism of addition of acetals to alkyl vinyl ethers [68,69].

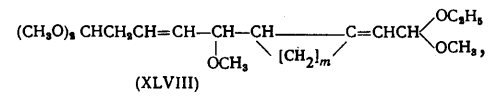
The condensation of glutaconaldehyde acetals [70,71] with 1-methoxybuta-1,3-diene, 1-ethoxypenta-1,3-diene, 1-ethoxy-2-methylbuta-1,3-diene, and 1-ethoxy-3-methylbuta-1,3-diene [29,66] has been studied. In every instance a mixture of telomeric compounds (XLVII), readily separable by fractional distillation, was obtained:



where $n = 1, 2, 3$; R = CH_3, C_2H_5; R^1, R^2, R^3 = H, CH_3.

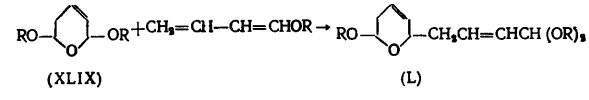
Alkoxyacetals of dialdehydes with 9, 13, and 17 carbon atoms in the chain were obtained according to this scheme.

Derivatives of a dialdehyde with six-membered ($m = 4$) and five-membered ($m = 3$) rings in the chain were obtained in the condensation of glutaconaldehyde acetals with 1-β-(ethoxyvinyl)cyclohexene and 1-β-(ethoxyvinyl)cyclopentene [66]:



where $m = 3$ or 4.

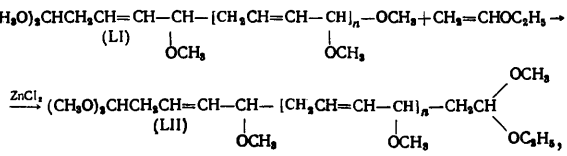
Although 1-alkoxydienes are capable of condensing with 2,6-dialkoxy-Δ^3-dihydropyranes (VLIX) [72] the yield of the condensation product (L) is low (17%) [65]:



where R = CH_3.

In their turn C_9- and C_{13}-alkoxydiacetals (LI; $n = 1$ and 2, respectively), obtained by the condensation of glutaconaldehyde acetal with 1-methoxybutadiene, are capable of reacting with ethyl vinyl ether to form alkoxyacetals

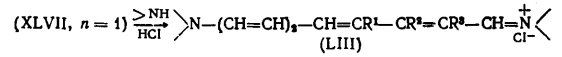
(LII), containing respectively 11 and 15 carbon atoms in the chain. The yield of (LII) is 41–43%:



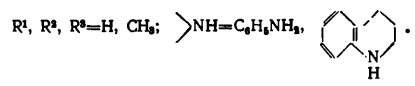
where $n = 1$ or 2.

The condensation examined is a simple general method for the synthesis of alkoxyacetals of unsaturated dialdehydes with 9, 11, 13, 15, or 17 carbon atoms in the chain.

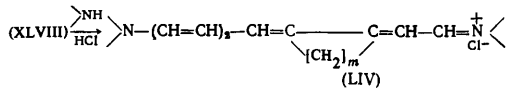
In the acid hydrolysis of the condensation products of glutaconaldehyde with 1-alkoxydienes (XLII; $n = 1$) in the presence of primary or secondary amines a δ-alkoxy-group is lost extremely readily, and cyanines (LIII) are formed in very good yield (up to 80%) [29,67]:



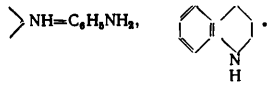
where



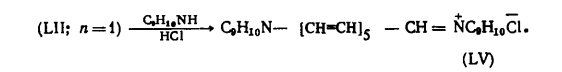
Cyanines (LIV) with six- and five-membered rings respectively in a conjugated chain [29] were obtained from alkoxydiacetals (XLVIII; $m = 4$ and 3)



where $m = 3$ or 4;

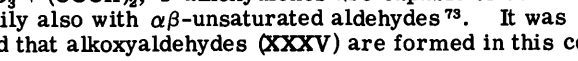


This method for obtaining cyanines was used for the synthesis of undecamethine compounds. Thus in the treatment of 1,3,7,11,11-pentamethoxy-1-ethoxyundeca-4,8-diene (LII; $n = 1$) with tetrahydroquinoline in dilute hydrochloric acid, bistetrahydroquinolide undecatetraenedial chloride [quinolinylundecapentaeneylidene quinolinium chloride] (LV) is formed in good yield [66]:



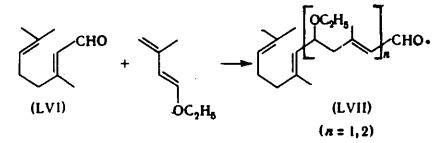
7. Condensation with αβ-Unsaturated Aldehydes

In the presence of catalysts such as BF_3, $ZnCl_2$, and $H_3BO_3 + (COOH)_2$, 1-alkoxydienes are capable of reacting readily also with αβ-unsaturated aldehydes [73]. It was found that alkoxyaldehydes (XXXV) are formed in this condensation:



which are readily converted into polyenals (XXXIV) on heating with phosphoric acid. 5-Ethoxycitral, 5,9-diethoxyfarnesal, octa-2,4,6-trienal, 3-methylocta-2,4,6-trienal, dodeca-2,4,6,8,10-pentaenal, and dehydrocitral were obtained in this way [73].

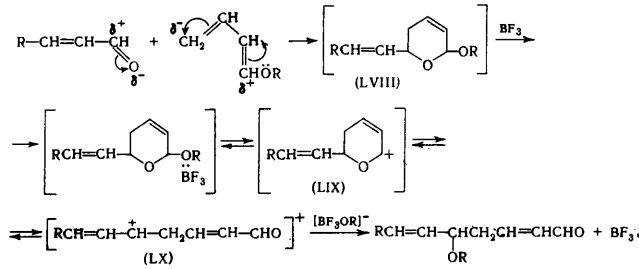
Citral (LVI) is also capable of undergoing this condensation, with the formation of terpene compounds [73] (LVII):



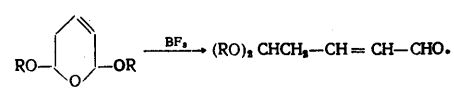
Furfural condenses rather readily with 1-ethoxybutadiene in the presence of the catalysts mentioned above. Here, as in other instances, a mixture of telomeric alkoxyaldehydes is obtained, which are then easily converted into furylpolyenals [73]. Unlike furfural, benzaldehyde condenses with 1-ethoxybutadiene with great difficulty, the yield of condensation product (5-ethoxy-5-phenylpent-2-enal) being ~ 10%.

β-Cyclocitral, 2,3-dihydro-2-methylbenzaldehyde, and also aliphatic aldehydes (butyraldehyde, isovaleraldehyde) seemed to be incapable of undergoing this condensation [73].

From our standpoint it seems most probable that the condensation of unsaturated aldehydes with 1-alkoxydienes is accompanied by the intermediate formation of dihydropyran (LVIII) as a result of a reaction of the diene synthesis type. Furthermore, the action of an acid catalyst, for example, BF_3, on (LVIII) produces an unstable carbonium ion (LIX), which then rearranges into the more stable αβ-unsaturated cation (LX). The reaction of (LX) with $[BF_3OR]^-$ leads to δ-alkoxyaldehydes of the (XXXV) type:



An indirect confirmation of this mechanism is the recent observation [53] of the rearrangement of 2,6-dialkoxy-Δ³-dihydropyrans into glutaconaldehyde monoacetal:



8. Reaction with Formylating Agents

In the reaction of 1-alkoxybutadienes with (chloromethylene)dimethylammonium chloride, obtained from dimethylformamide and carbonyl chloride (the Wilsmeier–Hagg reaction), Arnold [74] observed the formation of derivatives of glutaconaldehyde, which are cyclised in the reaction mixture under the action of ammonium salts into compounds of the pyridine series. It is interesting to note that such compounds are also formed by the acetals of crotonaldehyde and even by 1,1,3-trialkoxybutanes under the action of a formylating agent. This fact can evidently be explained only by the reaction of crotonaldehyde and

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1,1,3-trialkoxybutane acetals with the strongly electrophilic formylating agent producing intermediate 1-alkoxydienes, which also undergo formylation[74]:

$$CH_2=CH-CH=CHOR \xrightarrow{[(CH_3)_2N=CHCl]^+Cl^-} \rightarrow [(CH_3)_2N=CHCH=CHCH=CHOR]^+Cl^- \xrightarrow{OH^-} \rightarrow (CH_3)_2NCH=CH-CH=CH-CHO \xrightarrow{NH_4Cl}$$

Normant and Martin[24] made a detailed study of the formylation of some substituted 1-alkoxydienes with the aid of formylating agent from dimethylformamide and phosphoryl(V) chloride. This reaction gave a series of substituted unsaturated aminoaldehydes (LXI):

$$RCH=CR^1-CR^2=CHOC_2H_5 + [(CH_3)_2N=CHCl]^+[OPOCl_2] \rightarrow \rightarrow [(CH_3)_2NCHCl-CHR-CR^1=CR^2-CHOC_2H_5][OPOCl_2]^- \xrightarrow{-HCl} \rightarrow [(CH_3)_2NCH=CR-CR^1=CR^2-\overset{+}{C}HOC_2H_5 \longleftrightarrow (CH_3)_2\overset{+}{N}=CH-CR= =CR^1-CR^2=CHOC_2H_5][OPOCl_2]^- \xrightarrow{OH^-} (CH_3)_2N-CH=CR-CR^1=CR^2-CHO, \quad (LXI)$$

where R, R^1, R^2 = H or CH_3.

Normant and Martin[24] note certain features in the formylation of substituted 1-alkoxydienes. Thus with 1-ethoxy-3-methylbuta-1,3-diene the corresponding amino-aldehyde

$$(CH_3)_2N-CH=CH-CCH_3=CHCHO$$

could not be obtained. This is explained by the steric hindrance to electrophilic attack of the formylating agent by the terminal $CH_2=CCH_3$-group of the diene.

In the reaction of a formylating agent with 1-ethoxypenta-1,3-diene instead of the expected amino-aldehyde

$$(CH_3)_2NCH=CCH_3-CH=CHCHO \quad (LXII)$$

the amino-aldehyde

$$(CH_3)_2NCH=CHCH=CCH_3-CHO \quad (LXIII)$$

the structure of which was proved by the NMR method, was obtained. Normant and Martin[24] think that in the action of the formylating agent on 1-ethoxypenta-1,3-diene a carbonium ion normal for this diene salt is formed:

$$[(CH_3)_2N-CH=CCH_3-CH=\overset{+}{C}HOC_2H_5 \longleftrightarrow (CH_3)_2\overset{+}{N}=CH-CCH_3=CH-CH=CHOC_2H_5]$$

In the decomposition of this salt in alkaline medium initially the aminoaldehyde (LXII) is formed and also the dialdehyde

$$CHO-CCH_3=CHCH_2CHO \quad (LXIV)$$

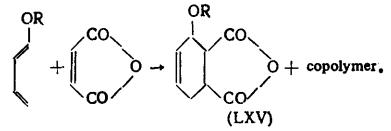
and dimethylamine (as a result of the hydrolysis of the excess of formylating agent). The dimethylamine liberated immediately reacts with the amino-aldehyde (LXII) and dialdehyde (LXIV) to form the isomeric cation

$$[(CH_3)_2NCH=CCH_3-CH=CHCH=\overset{+}{N}(CH_3)_2],$$

hydrolysis of which gives the more stable (LXIII).

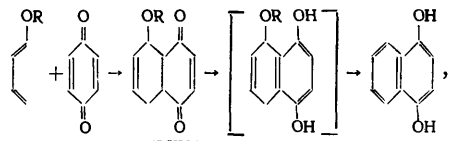
9. Diene Synthesis

The diene condensation of 1-alkoxybutadienes with maleic anhydride has been frequently studied[5,11,15,19,20,32,75,76]. Most authors[5,11,32,75] report that this reaction takes place very vigorously and leads to the formation of a normal addition product—the anhydride of 2-alkoxy-2,5,6-tetrahydrophthalic acid (LXV). Furthermore, the reaction is accompanied by the copolymerisation of 1-alkoxydiene with maleic anhydride:



(LXV)

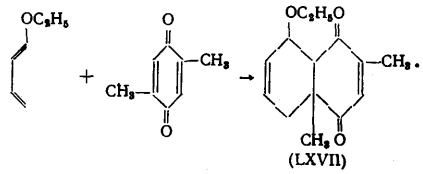
The reaction of 1-alkoxybutadienes with various quinones has been studied best. In the reaction of 1-methoxy- and 1-ethoxy-butadiene with *p*-benzoquinone addition products (LXVI) are formed, which lose alcohol under the influence of acetic acid and hydrogen bromide and are converted into 1,4-dihydroxynaphthalene[77]:



(LXVI)

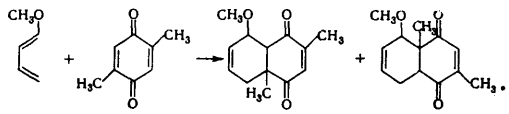
where R = CH_3, C_2H_5.

The reaction of 1-ethoxybutadiene with xyloquinone[78] gave only one isomer of the addition product, which was ascribed structure (LXVII) without proof:



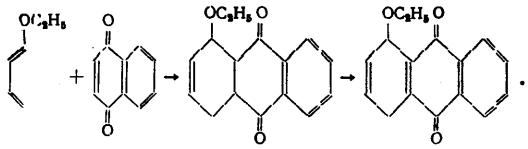
(LXVII)

The condensation of 1-methoxybutadiene with the same dienophile leads to a mixture of two structural isomers, the ratio of the amounts of *"ortho"* (LVIII) and *"meta"* (LXIX) isomers being 10 : 1:



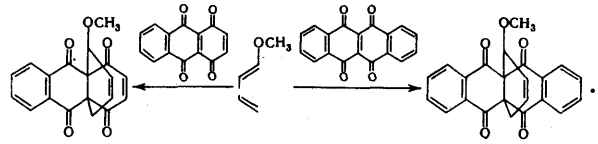
(LXIX) (LXVIII)

1-Ethoxybutadiene reacts readily with 1,4-naphthaquinone to form compound (LXX) which is readily oxidised by atmospheric oxygen to a dihydroanthraquinone derivative (LXXI)[11]:



(LXX) (LXXI)

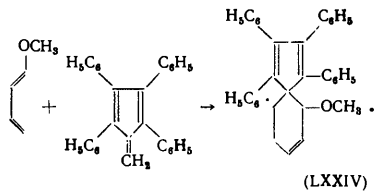
The condensation of 1-methoxybutadiene with quinizarin-quinone gives compound (LXXII) and that with tetracene-quinone gives compound (LXXIII)[79]:



(LXXII) (LXXIII)

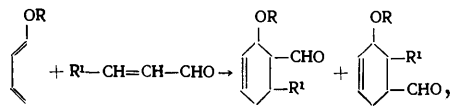
The condensation of 1-methoxybutadiene with tetraphenylfulvene gives an addition product (LXXIV) and in

condensation with tetraphenylpentadiene a substance whose structure has still not been explained is produced[80]:



(LXXIV)

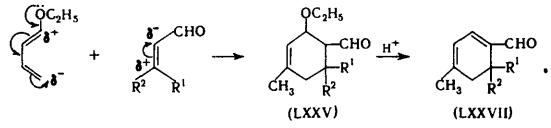
The diene condensation of 1-alkoxydienes with unsymmetrical dienophiles has been studied in a series of papers. Wichterle[1] was the first to condense unsaturated 1-alkoxybutadienes with acrylaldehyde and crotonaldehyde. He suggested that the addition products obtained contain both of the theoretically possible isomers:



where R^1 = H or CH_3. However, the structure of the addition products obtained was not proved.

The condensation of 1-cyclohexyloxybutadiene with crotonaldehyde was effected recently[5]. The authors, without giving any proof, consider that the addition product obtained is 3-cyclohexyloxy-2-methyl-1,2,3,6-tetrahydrobenzaldehyde (a *"meta"* adduct).

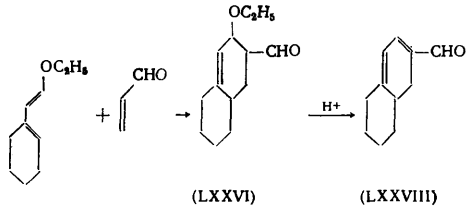
A special study[76] of the structural selectivity of the diene synthesis of 1-alkoxydienes with $\alpha\beta$-unsaturated aldehydes, revealed that the condensation of 1-ethoxy-3-methylbutadiene with acrylaldehyde, crotonaldehyde, and β-methylcrotonaldehyde leads to the formation exclusively of *"ortho"* addition products (LXXV) in accordance with the polarisation of the diene and dienophile:



(LXXV) (LXXVII)

The structure of the products (LXXV) was established chemically and by ultraviolet spectroscopy.

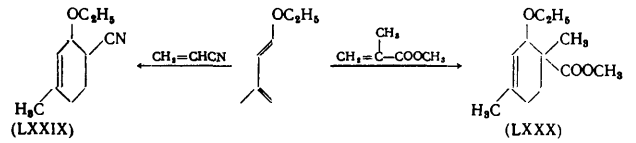
There is also structural selectivity in the reaction between 1-(β-ethoxyvinyl)cyclohexene and acrylaldehyde[76] with the formation of compound (LXXVI):



(LXXVI) (LXXVIII)

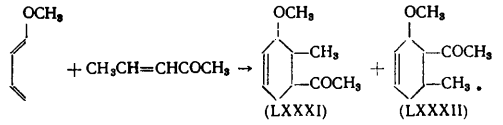
These reactions make accessible the cyclodialkenic aldehydes (LXXVII) and (LXXVIII) which are obtained by other methods in a much more complex manner.

1-Ethoxy-3-methylbutadiene readily undergoes a diene synthesis with acrylonitrile and methyl methacrylate to form 2-ethoxy-1,2,5,6-tetrahydro-4-methylbenzonitrile (LXXIX) and methyl 2-ethoxy-1,4-dimethylcyclohexene-3-carboxylate (LXXX). The reaction here is also structurally directed[76]:



(LXXIX) (LXXX)

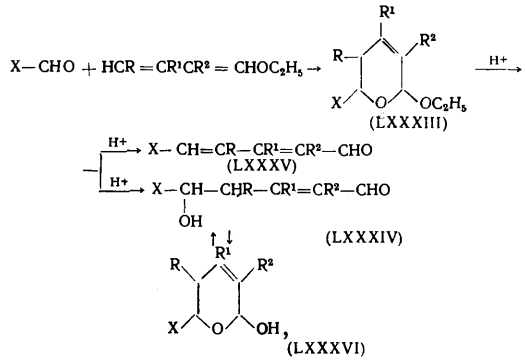
However, the condensation of methoxybutadiene with methyl propenyl ketone leads to a mixture of the two possible isomers (LXXXI) and (LXXXII)[81]:



(LXXXI) (LXXXII)

These isomers were separated by fractional distillation or (less successfully) chemically on the basis of the difference in activity of the carbonyl groups in the compounds (LXXXI) and (LXXXII) in the production of some of their derivatives.

The condensation of the 1-alkoxydienes with heterodienophiles has still been little studied. It was shown that 1-alkoxydienes are capable of undergoing a diene synthesis with paraform[82,83] and with aldehydes having electron-acceptor groups in the α-position—chloral and esters of glyoxylic acid[83]. In every instance the reaction leads to substituted 2-alkoxy-Δ^3-dihydropyrans (LXXXIII):

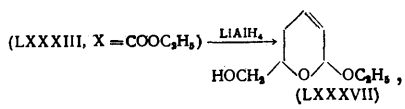


(LXXXIII) (LXXXV) (LXXXIV) (LXXXVI)

where X = H, $CCl_3COOC_2H_5$; R, R^1, R^2 = H, CH_3.

The hydrolysis of the dihydropyrans (LXXXIII) in acid medium allows either $\alpha\beta$-unsaturated δ-hydroxyaldehydes (LXXXIV) or ω-functionally substituted polyene aldehydes (LXXXV) to be obtained, depending on the reaction conditions. The compounds (LXXXIV) are in tautomeric equilibrium with their cyclic forms (LXXXVI).

6-Carboethoxy-2-ethoxy-Δ^3-dihydropyran (LXXXIII; X = $COOC_2H_5$) is readily reduced by lithium tetrahydroaluminate to give 2-ethoxy-6-hydroxymethyl-Δ^3-dihydropyran (LXXXVII) which is of interest as a starting material for the production of desoxysugars[83]:

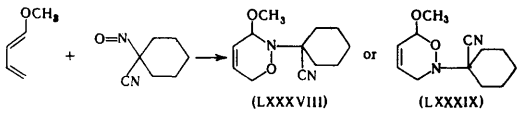


(LXXXVII)

where R^1 = R^2 = R^3 = H.

Finally, the condensation of 1-methoxybutadiene with 1-nitrosocyclohexanecarbonitrile has been described[84].

An addition product of structure (LXXXVIII) or (LXXXIX) is obtained in good yield:



(LXXXVIII) (LXXXIX)

10. Polymerisation of 1-Alkoxydienes

Due to the presence of an alkoxy-group, 1-alkoxydienes are rather strongly polarised and therefore tend mainly to ionic polymerisation. According to a patent[85] the polymerisation of 1-methoxybutadiene can be satisfactorily carried out in a reactor packed with kaolin. Clay, kaolin, hydrosilicates, etc. are used as catalysts, either pure or carried on silica gel or activated carbon. The solvents employed are petroleum ether, benzene, CCl_4, $CHCl_3$, etc. Liquid, viscous, and solid polymers were obtained in this way. Other authors[86] polymerised 1-methoxybutadiene using Ziegler catalysts: a polymer of crystalline structure was obtained, the infrared spectrum of which showed that it has a completely *trans*-structure.

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Lomonosov Moscow Institute
of Fine Chemical Technology

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Catalysis and Coordination Interaction

M.I.Siling and A.I.Gel'bshtein

The following topics are reviewed: catalyst activity and co-ordination power; influence of co-ordination on ligand reactivity; influence of ligands on the catalytic activity of metal ions; co-ordination interaction and characteristics of the transition state of the catalytic reaction. Because interactions of the co-ordination type occur frequently in catalysis, the experimental results and the theoretical concepts of co-ordination chemistry can be fruitfully applied to problems in catalysis: various approaches of this type are discussed. The important role of mixed complexes and of dative interaction in the mechanism of many catalytic reactions is stressed. 210 references.

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I. INTRODUCTION

The mechanism of catalysis is determined primarily by the nature of the intermediate chemical interaction between the reagent (R) and the catalyst (C). The following are the two cases most frequently met: the R–C interaction is covalent in character, i.e. σ-electrons are directly involved; the R–C interaction is of the coordination type, i.e. with the direct participation of unshared electron pairs or of π-electrons in vacant orbitals. This subdivision is similar to the classification proposed by Roginskii[1], according to which catalytic processes can be divided into two large classes: oxidation–reduction and acid–base, i.e. with or without the fission of an electron pair (homolytic and heterolytic processes respectively).

The assignment of the R–C interaction to the covalent or the coordination type is fairly arbitrary. Often, and particularly in complicated reactions, interactions of both types occur simultaneously. Yet, each of these two types of interaction shows some characteristic features, and it is therefore convenient to discuss them separately.

The specific features of the coordination type interaction (CTI) are favourable to catalysis. Thus, a good catalyst should interact rapidly with the reagents, it should thereby influence their reactivity profoundly, and it should be easily regenerated. The electrons involved in CTI are the least firmly bound (n- or π-electrons), their energy levels lying above the level of the bonding σ-electrons. Hence, the activation energy of the complex-formation reaction is usually small, leading to fast interaction. Furthermore, coordination can have a marked effect on the reactivity of the ligand. Thus, it has been shown[2] that molecules bound to the catalyst surface by a hydrogen bond or by a stable covalent bond do not undergo alcohol dehydration and ethylene oxide polymerisation reactions. The most favourable bond energy in this case is that of molecules bound by coordination forces to a surface metal atom.

It does not follow, of course, that the R–C interaction is of the coordination type in all cases of catalysis. First of all, the participating molecules do not always have n- or π-electrons, and catalysts (e.g., metals) sometimes lack the requisite electron-acceptor properties. Furthermore, CTI does not always effectively weaken the "required" bonds in the reactant molecules (i.e., those which must be broken during the reaction). Thus, although alcohol and amine molecules can undergo CTI, the stability of the C–H bond is not appreciably affected. These compounds are usually dehydrogenated on metallic catalysts. In this case the R–C interaction which is responsible for catalysis is probably of the covalent rather than the coordination type. Thus, CTI can be the predominant type of interaction in those cases of catalysis where the electronic structure of both the reactant molecules and the catalyst is conducive to it (by weakening the bonds to be broken in the reaction or by assisting the formation of new bonds). Many heterolytic reactions belong to this type of chemical process.

Homolytic reactions also involve, on occasions, a significant amount of CTI, particularly when individual atoms or ions act as the catalytically active centre. However, the specific surface effect arising from the presence of free electrons in the solid catalyst, which is of fundamental importance in many cases of heterogeneous catalysis, is obviously not a case of CTI.

Because of the frequency with which CTI occurs in catalytic processes[3–12], there is a need to apply the experimental results and the theoretical ideas of coordination chemistry to problems in catalysis. The important advances in coordination chemistry made during the last two decades give reason to expect a deep penetration into the science of catalysis of the theories and ideas developed for complexes.

II. CATALYTIC ACTIVITY AND COMPLEX-FORMATION FUNCTION

The relationship between complex-formation and catalytic properties of a substance is determined by two basic factors: the tendency to undergo CTI with the reactants and the influence of this interaction on the reactivity of the species involved in the catalytic reaction. To illustrate this statement, we consider the simple catalytic reaction

$$R_1 + C \overset{K}{\rightleftharpoons} R_1C$$

$$R_1C + R_2 \overset{K}{\rightleftharpoons} R_1R_2 + C$$

where K is the equilibrium constant of the first step, and k is the rate constant of the second (rate-limiting) step. If $K \ll 1$ the observed rate constant is

$$k_{obs} = Kk.$$

In this equation K expresses the affinity of the catalyst for R_1, and k depends on the reactivity of this reagent in the intermediate complex. In general:

$$k_{obs} = f(K_1,\ldots,K_n,k),$$

where $K_1, \ldots, K_n$ are constants which characterise the equilibria preceding the limiting step. The expressions for k_{obs} are in keeping with the well known principle that the catalytic activity of a substance cannot in general be defined by thermodynamic quantities only. The properties of the reactants in the intermediate complexes must also be considered. We shall examine each of these factors separately in the following subsections.

1. Catalyst Activity and Coordination Power

Catalytic processes consisting of a single elementary step have a low probability. A multi-stage reaction implies some affinity between the catalyst and at least one of the reactants. Hence, and in view of the frequent occurrence of CTI in catalysis, we may conclude that the catalytic activity of a substance should be related to its ability to coordinate to the reactants. Correlations of this type have frequently been reported: one example is shown in Fig. 1.

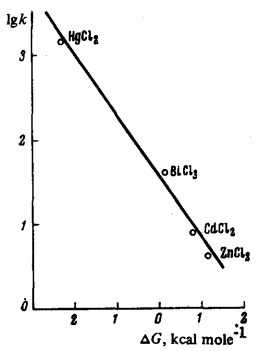


Figure 1. Catalytic activity of salts in the hydrochlorination of acetylene as a function of the stability of the catalyst–acetylene complex[46,47,167]: k is the rate constant for the reaction, ΔG is the free energy of formation of the $MCl_n.C_2H_2$ complex.

Information on the ability of the reactants to form complexes with various substances must obviously be of value in the selection of catalysts. The necessary data can be obtained, in the first place, from the accumulated fund of experimental material on the chemistry of complexes[13-19]. This approach to the problem of catalyst selection is subject to the following limitations: 1) existing data on the ability of reactants to form complexes with all the potentially useful catalysts are not sufficiently comprehensive; 2) the affinity of the catalyst for the reactant could be so low as to make an experimental study of the system excessively difficult; 3) the affinity could manifest itself only under conditions unfavourable to the study of complex formation.

The first of these limitations can be overcome to some extent by using published data on complex formation between the catalyst and some other compound, similar to the reactant in chemical structure. Strictly speaking, the molecules of the reactant and of the other compound should coordinate through the same functional group. The second and the third limitation should become less significant as more refined experimental techniques are developed. Lastly, all the limitations can be circumvented in principle by using theoretical ideas to evaluate the coordination power of a compound. Modern theories of the chemical bond in complexes (such as the valence bond theory, the crystal field and ligand field theories) allow useful though essentially qualitative predictions to be made of the possibility of coordination and of the stability of the coordinate bond. This problem has been discussed in a number of monographs and review articles[18-26,205]. Various semi-empirical relationships between the stability of the complex and characteristics of the central ion and of the ligand such as charge, ionisation potential, electronegativity, electron affinity, and polarisability can also be used[16,18,27-31].

Direct interaction between the catalyst and each of the reactants must, of course, be conducive to effective catalysis in multimolecular reactions, since it weakens the appropriate bonds of all the reacting molecules. Furthermore, the fixation of two or more reactant molecules close to an atom (or ion) of the catalyst can give rise to conditions which are sterically more favourable to interaction. In their discussion of the mechanism of enzyme action Braunshtein and coworkers[32] show that the formation of an intermediate complex (involving oriented contact of the reactants) produces a drastic increase in rate because low-probability, high-order reactions are replaced by first-order reactions. According to Bender[33], complex formation between the catalyst and both reactants can favour a bimolecular reaction by increasing the entropy of activation. Bender[33] and Eichorn[34] also point out that electrostatic repulsion should be minimised in the complex formed by a positively charged catalyst with nucleophilic reactants.

The above considerations justify the assumption that interaction between the catalyst and each of the reactants is involved in the mechanism of many catalytic reactions. In the case of CTI, mixed complexes may be formed. We shall consider a number of results which confirm the importance of mixed complexes in catalysis.

If the ability of the catalyst to coordinate to both reactants is important in many types of bimolecular catalystic reaction, compounds of metals able to form complexes with a wide variety of ligands should be the most effective catalysts. Grinberg[19] characterised the tendency of an element to form complexes in terms of the number of ligand types with which complexes are formed. In this sense, the Group VIII elements and the Cu, Zn, and Cr subgroup show the highest tendency to form complexes. These same elements, and their compounds, are found to catalyse many types of reaction.

There is experimental evidence that the mechanism of various enzyme processes involves the formation of mixed complexes between the enzyme and both reactants[35,36].

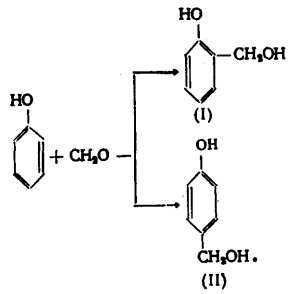
Flid and coworkers[37-43,53,54], and Gel'bshtein and coworkers[12,44-52], have studied in detail the addition of HX molecules to acetylene (where X = OH, Cl, CH_3COO). The reactions were catalysed by salts of metals of the Zn and Cu subgroups. It was found that these reactions involve, as an intermediate step, the formation and the transformation of a mixed complex (C_2H_2.catalyst.HX). The most convincing argument in favour of this mechanism is the experimentally established fact that the catalyst forms complexes both with C_2H_2 and with HX under the conditions of the reaction[12,43,45,46,51-54].

The retardation of various reactions by one of the reactants and the relationship between the coordination number of the metal atom or ion and its activity can be explained in the light of the role of mixed complexes in the mechanism of catalysis. Formation of the mixed complex is hindered when the catalyst shows too great a tendency to coordinate to one of the reactants, because all the free sites in the coordination sphere are occupied by one of the participants in the reaction. In this case the rate of the reaction can decrease as the concentration of this reactant increases. (This phenomenon, known as substrate retardation, is typical of many enzyme reactions[36].) A study of the kinetics of the vapour-phase synthesis of vinyl acetate from acetylene and acetic acid[48,51,55] has shown that the reaction is retarded by an excess of acetylene when catalysed by mercuric acetate, and by acetic acid when cadmium or zinc acetate are used as the catalyst. It has been suggested that the retardation arises from the formation of a complex between the catalytic salt and two molecules of one of the reactants, which prevents the formation of the mixed complex. This hypothesis was confirmed by adsorption measurements[12,50], according to which mercuric acetate can form a complex with two molecules of C_2H_2 under the conditions of the reaction, whereas zinc and cadmium acetates form complexes with two molecules of CH_3COOH. Order-of-magnitude agreement was obtained between the complex-formation constants of the catalytic salts with acetic acid calculated from the kinetic data by assuming the above mechanism[48,55] and the values determined from adsorption measurements[12,50].

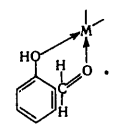
The smaller the number of free sites in the coordination sphere of a metal ion playing the part of the catalytically active centre, the lower will be its power to coordinate reactants, and in particular its power to form mixed complexes. This explains the known fact that the activity of an ion decreases, as a rule, as its coordination number increases. The effect is observed in a variety of catalytic reactions, for example in the decomposition of hydrogen peroxide catalysed by various catalase models[56], in the cracking and dehydration reactions of isopropanol on naturally occurring aluminosilicates[57], and in the solvolysis of fluorophosphates catalysed by various metal chelates[58].

The reactant molecules in the mixed complex take up well defined relative orientations: this effect can often lead to high catalytic specificity. According to Thompson and Busch[59], the coordination sphere of the metal ion can act as a matrix for the reaction, by imposing strictly defined positions on the reacting groups and thus controlling highly selective multistage reactions. The importance of the matrix function of the catalyst has been stressed by Roginskii[60].

The reaction between phenol and formaldehyde, giving saligenin (I) and *p*-hydroxybenzyl alcohol (II) as primary products, is a good illustration of the influence of mixed complex formation on the selectivity of the reaction:



When the reaction is catalysed by a proton acid (pH 1–2) the two phenolic alcohols are formed in approximately equal amounts[61,62]. On the other hand, catalysis by some metallic salts (such as zinc acetate) leads almost exclusively to the formation of saligenin[63,64]. This effect can be easily explained by postulating an intermediate mixed complex (III) whose spatial configuration favours reaction in the *ortho*-position:



(III)

The synthesis of phenolic alcohols belongs to the large group of heterolytic reactions which are accelerated both by proton acids and by aprotic (Lewis) acids. The observed differences in the catalytic action of the two types of acid can be ascribed to various causes, intimately related to the complex-formation properties of the catalyst. The proton is catalytically more active than aprotic acids in a number of reactions[9,58], but the opposite can also be true. Thus, the esters and amides of α-aminoacids are hydrolysed much more rapidly in the presence of Cu^{2+} ions than in the presence of hydrogen ions[65]. The catalytic activity of Hg^{2+}, Cd, Zn, and Bi chlorides supported on active carbon towards the hydrochlorination of acetylene in the vapour phase is much greater than that of HCl adsorbed on the carbon surface[47]. The liquid-phase hydration of acetylene proceeds quite rapidly in the presence of mercuric chloride, but it not catalysed to any extent by proton acids[37-40]. Many examples of this type could be quoted.

The very high activity of proton acids towards many reactions is evidently associated with the extremely small radius of the proton (10^{-13} cm), which is smaller than the typical radius of metal ions by 5 orders of magnitude. As a result, the proton is characterised by a high polarising effect as well as negligible steric hindrance.

The higher activity of aprotic catalysts in a number of cases is more difficult to explain. Many workers stress the greater positive charge of the metal ion[34,66], but this factor does not seem to be the essential one to the present writers. The electron-acceptor and the polarising power of a cation are determined by the parameters z/r and z/r^2, which involve the radius as well as the charge of the ion. It is obvious that the value of these parameters must be higher for the proton than for any metal ion, even

multiply charged. Furthermore, it now appears unlikely[67] that the metal ion in a catalyst structure carries a high positive charge.

Many workers[7,33,68,69] ascribe the high activity of Lewis acids (as compared with the proton) to the ability of a metal ion to coordinate to several reactants (or two groups in the molecule of a single reactant) at the same time. This view is consistent with the suggested importance of mixed complexes in catalysis.

Another possible explanation of the high catalytic activity of aprotic acids towards certain reactions should be mentioned. A large group of metal ions can exhibit electron-donating as well as electron-accepting properties in CTI, a function of which the proton is quite incapable. When activation of the reactant is mainly by dative C–R interaction we can expect metal cations liable to this type of interaction to show significantly higher catalytic activity than the proton. The acetylene addition reactions considered above are an example of this type of system.

2. Influence of Coordination on Ligand Reactivity†

In this section we shall discuss the influence of CTI between catalyst and reactant on the ability of the latter to undergo chemical change. Data on the reactivity of coordinated ligands should be relevant to this problem, whether an intermediate complex is formed during the catalytic reaction or whether CTI is confined to the transition state.

Coordination causes redistribution of the electron density in the ligand molecule, alters the interatomic distances and the bond angles, and therefore affects the polarity and the stability of the bonds. In general, therefore, coordination cannot fail to influence the reactivity of the ligand. Usually (but not invariably), the bonds nearest to the coordination bond are weakened. Coordination due to interaction between non-bonding electrons of the ligand and vacant orbitals of the metal atom shifts the electron density within the ligand molecule towards the central atom of the complex. As a result, the coordinated molecule becomes more electrophilic than the free ligand.

The situation becomes more complicated when dative interaction (leading to transfer of negative charge in the opposite sense, from the central atom towards the ligand) contributes significantly to the formation of the coordination bond. However, it does not follow that formation of a dative π-bond must weaken the influence of coordination on the reactivity of the ligand. When a double bond is formed between the metal and the ligand the disturbance caused by coordination extends over a greater number of electrons. Under these conditions the antibonding orbitals of the ligand become involved, and substantial weakening of some of the bonds within the coordinated molecule can ensue. Orgel[24] states that "the combined effect of two bond-formation mechanisms is much greater than the sum of the separate effects, because each mechanism removes the unfavourable charge accumulation due to the other".

The following are some of the most important sources of information on the reactivity of ligands in complexes: 1) data on the chemical reactions of coordinated molecules. (Unfortunately, very few data of this type are as yet available.) 2) infrared spectral data on the complexes. (The decrease in the force constant or the lowering of the stretching vibration frequency for a particular bond in the ligand molecule resulting from coordination can be taken as an approximate measure of the relative weakening of that bond.) 3) the effect of coordination on the E–H bond (where E = O, N, S, Cl, etc.) can be assessed by using relative data on the acid ionisation constant of the complex and of the free ligands. (The acid–base properties of complexes have been discussed in detail by Grinberg[19].) 4) indirect evidence on the influence of CTI on ligand reactivity can be obtained by comparing the catalytic activities of various substances in reactions involving the ligand in question.

We shall discuss the influence of coordination on the tendency of ligands to undergo chemical change by considering groups of ligands of a given type. This approach should be fruitful because it allows us to apply existing data to the problems of catalysis, and in particular to catalyst selection and the mechanism of catalysis.

Amines

Amines coordinated through the lone pair of electrons on the nitrogen atom show a weakening of the N–H bond, which manifests itself in an enhancement of the acidic properties of coordinated amines[19]. For example, the ionisation constants of complexes with imidazole derivatives are higher than those of the free ligands by 3–4 orders of magnitude[70–72]. The large drop in the N–H stretching vibration frequency observed[73–77] in the infrared spectra of the complexes (as compared with the uncoordinated amines) is consistent with these results. In complexes with different metals this frequency decreases as the stability of the complex increases. Thus, a study of the infrared spectra of aminoacid complexes with various bivalent metals[77] has shown that ν_{N-H} for the complexes is consistently lower than for the sodium salts of the aminoacids. The authors ascribe this frequency shift to an increased positive charge on the nitrogen on formation of the M–N bond, resulting in a decrease of the N–H force constant in proportion to the strength of the M–N bond, i.e. to the stability of the complex. According to Filimonov and Bystrov[76], the strength of the N–H bond in the coordinated amine is influenced not only by the lower electron density on the nitrogen atom, but also by the change in hybridisation of the nitrogen valency orbitals resulting from coordination. It has been pointed out[74,75] that hydrogen bond formation between a coordinated amine and an anion in the outer sphere of the complex can also weaken the N–H bond and shift its absorption band towards lower frequencies.

Several workers have studied the reactions of ammines. Chugaev[78] showed that HCl is eliminated from chloropentammineplatinum(IV) chloride under the influence of alkali:

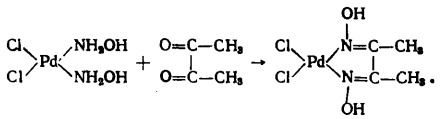
$$[Pt(NH_3)_5Cl]Cl_3 + NaOH \rightarrow [Pt(NH_3)_4NH_2Cl]Cl_2 + NaCl + H_2O.$$

Grinberg and Gil'dengershel' found[79] that ethylamine molecules in the inner sphere of a Pt^{4+} complex can be hydrolysed to ethanol and ammonia, the latter remaining coordinated to the platinum. Very drastic conditions are needed to hydrolyse free aliphatic amines, and hence we may conclude that coordination weakens not only the nitrogen–hydrogen but also the nitrogen–alkyl bond. Kukushkin[80–84] has made a detailed study of the chlorination of ammonia bound in various Pt^{4+} complexes, and found that the rate constant for coordinated ammonia can be higher or

†For a review of the early work, mainly up to 1940, the reader is referred to Ref. 3.

lower than for the ammonium ion, depending on the charge of the complex ion and on the nature of the ligands.

It has been reported[85] that coordinated hydroxylamine can be condensed with α-diketones with formation of dioximes;



Activation of the N–H bond as a result of CTI should evidently be noticeable in the catalysis of specific amine reactions by Lewis acids. Reactions of this type include the interaction of amines with ketones (catalysed by Zn and Cd salts[4]), the synthesis of mono-, di-, and trimethylamines from ammonia and methanol over alumina, the synthesis of flavanthrone by condensation of 2-aminoanthraquinone in the presence of $SbCl_3$, used in the production of dyestuffs, etc.

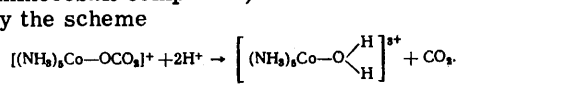
Oxygen-containing ligands. The coordination of ligands through an oxygen atom usually weakens the bonds adjacent to M–O. It is well known that complex formation increases the acidity of oxygen-containing molecules[19,86–88]: for example, the acidic ionisation constant of the aquo-ions of various metals is several orders of magnitude higher than the value for water. This is consistent with the observation[74] that the stretching vibration frequency of water is drastically decreased by coordination.

The spectra of the complexes of ligands containing carbonyl groups, such as ketones, esters, salicylaldehyde, tropolone, etc., have been studied intensively[73–75]. As a rule, coordination lowers the frequency of the C=O stretching vibration, obviously because the multiplicity of the bond is lowered by the shift of the π-electron cloud towards the oxygen atom[74]. The parallelism between this lowering of frequency and the stability of the complex has been repeatedly stressed.

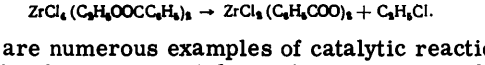
Nakamoto's analysis[75], of the infrared spectra of metal acetylacetonates leads to the conclusion that coordination of acetylacetone causes a weakening of the C–C as well as the C–O bond. It has been stated[73–75] that coordination of the carboxylate anion $(R-C\overset{O}{\underset{O}{<}})^-$ produces a lowering of the stretching vibration frequency for one of the C–O bonds, whilst at the same time increasing the frequency for the other C–O bond. Thus, the coordinated carboxyl group approximates to the structure $-C\overset{O}{\underset{O^-}{<}}$, characteristic of esters.

The weakening of the bonds adjacent to the coordination bond produced by complex formation is made evident by the reactions of oxygen-containing ligands. Meerwein and Hinz[89] had found, as long ago as in 1930, that butyl methyl ether is formed when diazomethane is passed through solutions of some salts ($ZnCl_2$, $FeCl_3$, etc.) in butanol. Free butanol does not undergo this reaction. Meerwein therefore suggested that dissolution of these salts in the alcohol involves the formation of complexes of the $\begin{matrix}R\\H\end{matrix}\!\!>\!O\ldots MX_n$ type.

Hunt and coworkers[90] showed, using ^{18}O, that the Co–O bond is not broken during acid hydrolysis of carbonatopentaamminecobalt complexes, and that the reaction occurs by the scheme



Phenyl esters complexed with $AlBr_3$ split off alkyl bromide when heated in benzene, and are subsequently hydrolysed to phenol by water[91]. Benzoate esters complexed with Hf or Fe chlorides undergo thermal decomposition with evolution of alkyl chloride[92,93]. For example,

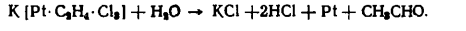


There are numerous examples of catalytic reactions in which CTI between a metal ion of the catalyst and an oxygen atom of the reactant plays a mechanistically important role. There is little doubt that the weakening effect of this interaction on the O=C, O–C, O–H bonds and also on their neighbouring bonds is one of the key factors in many catalytic reactions. Typical of these are the decarboxylation of keto-acids, catalysed by various metal ions[94,95], the dehydration of acids and alcohols[2,96] over Al_2O_3, the Friedel–Crafts alkylation and acylation of aromatic compounds, the synthesis of phenol–formaldehyde resins of the *ortho*-Novolak type[63,64,97], the hydrochlorination of methanol on metal chlorides[98] (Cd, Zn, and Bi), and others.

Alkenes and alkynes. A considerable amount of work has been done on the coordination of olefins and acetylenes, and several review articles have been published[99–104]. Dewar[105,106] has suggested that coordination of unsaturated compounds involves the interaction of π-electrons from the ligand with vacant orbitals of the metal ion, as well as dative interaction between *d*-electrons from the metal and antibonding π-orbitals of the ligand. Experimental confirmation of Dewar's views has recently been obtained (see Ref. 104), and these views are now generally accepted. Thus, the metal ion in general shows both acceptor and donor properties in the coordination of unsaturated ligands. Because of the acceptor and donor behaviour of the central ion of the complex, the electron population of the bonding π-orbitals of the ligand decreases, and the population of the antibonding orbitals increases. Hence, the coordination of unsaturated compounds at a carbon–carbon multiple bond should cause weakening of this bond. Many workers have in fact reported a significant lowering of the stretching vibration frequency of a multiple bond as a result of complex formation: for example, in studies of the Ag^+ complexes with alkenes and alkynes[107,108], of compounds of the Zeisse's salt type[109–111], of the acetylene complexes of copper and platinum[112,113], and others (see Refs. 73–75).

In some systems, coordination also weakens the =C–H and ≡C–H bonds. The acidic properties of acetylene and vinylacetylene are enhanced by complex formation with Cu(I) salts[114,115]. Temkin[43] made an analysis of the published data on the excited states of acetylene, and concluded that dative interaction has a profound effect on the weakening of the C–H and C≡C bonds.

The activation of olefins on coordination is reflected in the reactions of many platinum complexes[103]. Thus, bromine reacts with olefin complexes to form bromosubstituted olefins. The ethylene complex is rapidly and quantitatively reduced by hydrogen at room temperature with formation of ethane. Zeises's salt is decomposed by hot water according to the equation



A similar reaction occurs also with the ethylene complexes of platinum[116,129].

CTI plays an important part in determining the mechanism of the catalytic reactions of alkenes and alkynes. We

need mention only the reactions of olefin polymerisation[117-126], oxidation of ethylene to acetaldehyde[127-134], and acetylene addition reactions[37-55]. Many workers[12,40-43,47-52,135] have stressed the importance of dative interaction in the catalysis of the reactions of unsaturated compounds.

Aromatic compounds. Coordination interaction between aromatic hydrocarbons and metal cations can arise through the π-electron system of the hydrocarbon. The possible role of the resulting π-complexes in electrophilic substitution reactions has been exhaustively discussed in the literature (see, for example, Refs. 136 and 137). A great deal of work[138,139] has been done on the ArH–HX–MX system, where X = halogen.

Recent work[140-144] has led to the hypothesis that the π-complexes of aromatic hydrocarbons with metallic or oxidic catalysts can play the role of intermediates in catalytic reactions. Thus, Völter[143] suggests that the hydrogenation of alkylbenzenes on Ni–MgO catalysts involves the formation of π-complexes between the hydrocarbon and the catalyst, which are then hydrogenated by adsorbed hydrogen atoms.

Existing data are not sufficient to justify a definite conclusion on the role of CTI in determining the reactivity of aromatic hydrocarbons. We may assume that the effect does occur, and results in a slight decrease in reactivity towards electrophilic reagents. Data on the chemical reactivity of complexes of the ferrocene and dibenzene-chromium type are of little help, because we still lack general rules as to the behaviour of these compounds[145-147]. Thus, ferrocene is more reactive than benzene towards electrophilic substitution, a behaviour diametrically opposite to that of the dicyclopentadienyl complexes of other metals.

Jones and coworkers[148-153] studied the effect of coordination on the reactivity of aromatic ligands containing nitrogen or oxygen atoms. The reaction rate was significantly affected by complex formation in only a few cases. Thus, a study of the rate of nitrogen coupling of 8-quinolinol-5-sulphonic acid and of its Zn^{2+} complex showed[151] that the free phenate ion reacts 10^4 times faster that the same ion coordinated to the zinc ion, but the latter is significantly more reactive than the undissociated ligand. Inner complexes of 8-quinolinol with Fe^{3+}, Cr^{3+}, and Co^{3+} are brominated 35 times faster than the free ligand[153]. On the other hand, it is stated[148] that the activity of aniline and pyridine towards electrophilic reagents is the same whether the bases are free or coordinated to Cr^{3+}. Jones' general conclusion is that coordination of simple aromatic ligands has a relatively minor effect on their reactivity towards electrophilic agents. Two papers[154,155] are quoted in support of this conclusion. In the former, the π–π^* transition in the electronic spectrum of pyridine is shown to be relatively insensitive to coordination. In the latter, the π-electron density on the atoms of the porphin ring was calculated and shown to be little influenced by complex formation with Fe(II)

Jones also concluded[152] that the direction of electrophilic substitution reactions of aromatic compounds is not affected, as a rule, by coordination. The present writers consider, however, that coordination can influence the isomeric composition of the products of electrophilic substitution when both species involved in the reaction can undergo CTI with the catalyst. The reaction between phenol and formaldehyde discussed above (p. 484 of Russian; p. 11 of translation) is an example of this type of behaviour.

Hydrogen halides. Coordination increases the polarity of the bond in the hydrogen halide (HX) molecule. The cations of many metals, and in particular those of the platinum group and of the copper and zinc subgroups, can coordinate to HX with formation of $H_n[MX_m]$ acidocomplexes, in which the hydrogen is located in the outer sphere of the complex as a proton[15-17,19,156,157]. Complexes of this type are formed not only in solution, but also in molten salts[158,159], and on surfaces[12,46].

Ahrland[160] suggested the formation of a dative π-bond between M and X, by the interaction between the d-electrons of the metal and the free d-orbitals of the halogen, in order to explain many experimental observations on the stability of halogeno-complexes[16,18]. This hypothesis is consistent with the report[157] that the cations of certain metals (alkali, alkaline-earth, tervalent rare-earth, and some others) which have no mobile d-electrons cannot readily form negatively charged complexes with the chloride anion. On the other hand, cations prone to dative interaction (e.g. Pt, Pd, Hg, Ag) form complexes of this type over the whole of the HCl concentration range.

The polarising and weakening effect of CTI on HX molecules is relevant to the catalysis of many reactions involving hydrogen halides. We may mention, as an example, the hydrochlorination reactions of acetylene[47,49,51] and methanol[98], catalysed by Hg^{2+}, Cd, Zn, and Bi chlorides.

Carbon monoxide. The drastic change in reactivity resulting from the coordination of carbon monoxide was first observed by Hieber and coworkers[161,162] in the early 1930's. The ease of oxidation in particular, of CO is very much increased by coordination. The following are typical reactions:

$$PtCl_2CO + H_2O \rightarrow Pt + CO_2 + HCl$$
$$Fe(CO)_5 + 2NH_3 + H_2O \rightarrow H_2NCOONH_4 + H_2.$$

According to currently-held views, CO takes place in CTI not only as a donor but also as an acceptor of electrons[24,163,164]. Dative interaction, made possible by the free antibonding π-orbitals of the ligand, contributes very significantly to the stability of the resulting carbonyl complexes. This is confirmed by the fact that carbon monoxide forms complexes with many transition metals but not with the usual acceptors of unshared pairs such as BF_3.

Coordination of carbon monoxide decreases the stability of the C–O bond. Thus the C–O stretching vibration frequency is significantly lowered on going from free carbon monoxide to carbonyl complexes[75,164]. The dative component contributes significantly to the loosening effect of CTI on the C–O bond. Markov and Fasman[165] studied the mechanism of the catalytic activation of CO in solutions, and concluded that dative interaction between the metal and carbon monoxide is one of the necessary conditions for activation.

The influence of CTI on the reactivity of carbon monoxide is shown by the many catalytic reactions involving metal carbonyls (e.g., oxo-synthesis reactions).

Nitrogen. The activation of molecular nitrogen due to CTI is discussed at length in a recent review article by Vol'pin and Shur[166].

Oxygen. The possibility of CTI between metal ions or atoms and the O_2 molecule has been considered by many authors[9,11,68,163]. According to Jones[11], activation of molecular oxygen by coordination should be widespread in inorganic and in biological systems. He suggests that

the cations which are most active in this respect are characterised by a tendency to form π-bonds and to transfer an electron to the oxygen. These properties are found in Fe^{2+}, Mn^{2+}, Co^{2+}, and Cu^{+}.

A coordinate bond involving a dative component can be realised in the ions FeO_2^{2+} and CuO_2^{+}, which play an important role as oxygen carriers in the activity of some enzymes[168]. Orgel[24] mentions oxyhemoglobin, oxymyoglobin, and other biologically important compounds of iron, copper, and cobalt as examples of oxygen-containing complexes. Griffith[169] considers the bond between O_2 and iron in the hemoglobin complex to be similar to the Pt–ethylene bond in the Zeise salt (see Refs. 74 and 104).

It can be assumed that an oxygen molecule is held by a coordinate bond in the molecule $[IrCl(CO)O_2(PPh_3)_2]$, where $Ph = C_6H_5$. The structure of this product, prepared by Vaska[170] by treating the complex $[IrCl(CO)(PPh_3)_2]$ with molecular oxygen, has been investigated[171]. The oxygen atoms were found to lie at the same distance from the iridium atom, the length of the O–O bond (1.30 Å) being close to the distance between oxygen atoms in the O_2^- ion (1.28 Å).

Hydrogen. The activation of molecular hydrogen by metal ions has been discussed in a number of papers[172-176]. Interaction between an H_2 molecule and a metal ion or atom may involve attraction of the electrons from the hydrogen towards the free orbitals of the metal, and dative interaction between the *d*-electrons of the metal and the antibonding orbital of the hydrogen[163,177]. Strictly speaking, only the latter should be termed CTI, since the σ-electrons of the H_2 molecules are involved in the former.

Bykhovskii and Temkin[177] consider dative interaction to be an essential part of the mechanism of molecular hydrogen activation in homogeneous catalysis. Arguing against Halpern's suggestion[172] that the activation of H_2 is determined primarily by the electron-acceptor properties of the metal, these workers point out that the bond order in the H_2 molecule and the H_3^+ and H_3^- ions is consistent with a considerable loosening of the H–H bond, resulting from the transfer of an electron to the antibonding orbital of the hydrogen molecule. Gupta's[178] quantum-mechanical calculation for the H_2^- ion lends support to this view.

Hydrido-complexes, such as $[IrH_2Cl(CO)(Ph_3P)_2]$ [179] and $\{PtHCl[P(C_2H_5)_3]_2\}$,[180] have recently been prepared. The nature of the metal–hydrogen bond in these compounds is evidently the same as in covalent metal hydrides[179]. According to Halpern[174], the mechanism of the catalytic activation of hydrogen often involves the formation of intermediate hydride complexes in which the hydrogen can be treated as an anionic ligand.

III. INFLUENCE OF LIGANDS ON THE CATALYTIC ACTIVITY OF METAL IONS

The catalytic properties of a metal ion are often substantially influenced by the nature of the ligands. Halpern[173] has obtained data which characterise the relative influence of various complexing agents on the activity of the Cu^{2+} ion in homogeneous hydrogenation reactions (see Table).

It is reported[181] that the reactivity of platinum complexes towards the CO oxidation reaction decreases along the following series of ligands:

$$I > Br > CNS > Cl > NO_2 > OH > NH_3 > CN.$$

Replacement of the chloride by the citrate anion in the coordination sphere of the Ru^{3+} complex causes a significant increase in the catalytic activity of the complex towards the oxidation of ethylene and acetaldehyde[182].

Terent'ev and Mogilyanskii found[183-185] that aromatic amines in a pyridine solution in the presence of Cu_2Cl_2 are oxidised by atmospheric oxygen to diazo compounds. The catalyst in this case is a pyridine complex of the copper salt. On replacing the pyridine by 2-methylpyridine the reaction proceeds much more slowly, and if quinoline, dioxan, or alcohol are used as solvents no oxidation is observed.

Influence of complexing agents on the catalytic activity of the Cu^{2+} ion.

Agent	Relative catalytic activity	Agent	Relative catalytic activity
Perchlorate	1	Sulphate	6.5
Butyrate	150	Chloride	2.5
Propionate	150	Glycine	0.5
Acetate		Ethylenediamine	0.1

The nature of the ligands has a particularly strong influence in the case of enzymes and their models. The catalase activity of lead ions complexed with various Schiff's bases is almost 300 times higher than the activity of the simple lead ion[186]. The activity increases by several orders on going from the hydrated iron ion to an albumin–porphyrin complex of iron[187]. Many examples of this type are quoted by Langenbeck[188] and Nikolaev[189,190].

Often the nature of the ligand affects the direction of the reaction as well as the activity of the metal-containing catalyst. The emulsion polymerisation of butadiene in the presence of K_2PdCl_6 gives mainly a 1,2-polybutadiene structure, whereas the 1,4- polymer is the main yield when PdI_2 is used as catalyst[191]. Depending on the coordination sphere of the nickel complexes used as catalysts the polymerisation of acetylene can yield benzene or cyclooctatetrene[192].

To explain the influence of ligands on the catalytic properties of complexes, several factors must be considered. The tendency of catalysts to form complexes with ligands, and the influence of CTI on their reactivity, are determined first and foremost by the acceptor and donor properties of the metal ion. Hence, these properties must also to a large extent determine the catalytic activity of the complex. The nature of the metal–ligand bond has a profound effect on the donor–acceptor properties of the central atom. As the ionicity of this bond increases, the acceptor tendency of the metal ion increases and the donor tendency decreases. Formation of dative bonds increases the positive charge on the central atom and thus enhances its acceptor properties.

In mixed complexes, the ability of some of the ligands to undergo dative interaction results in a loosening of the dative bonds between the metal and the other ligands. In this case, the ligands are competing for the *d*-electrons of the metal. If dative interaction is needed to activate the reagents, a good catalyst will not include ligands capable of forming dative bonds.

These considerations can be used to analyse the effect of the carrier on the activity of the catalyst when CTI between the metal ion (or atom) and the carrier can be assumed. We have used this approach[12,49,51,52] in our work on vapour-phase addition reactions to acetylene to explain the fact that salts are more active when deposited on carbon than on other carriers. We were able to conclude that carbon, as a ligand, can enter into donor–acceptor interaction with a metal ion, playing the part of an electron donor. As a result, the donor properties of the cation and its tendency to undergo dative interaction are enhanced: this is a very significant factor in determining the activation of acetylene.

The crystal field theory can be used to discuss the role of the carrier. Erofeev and coworkers[193] have suggested an interaction between the atoms or ions of the deposited metal and the crystal lattice of the carrier, resulting in penetration of the metal ions into the surface layer of the carrier. On this assumption, they were able to explain why γ-Al_2O_3 is the best carrier for nickel hydrogenation and dehydrogenation catalysts and for chromium oxide dehydrocyclisation catalysts. The structure of γ-alumina is such that the Cr^{3+} and Ni^{2+} ions find themselves in an octahedral field, which offers a higher stabilisation energy than fields of different symmetry.

Unusual oxidation states for particular metals can often be stabilised by complex formation. Thus, complexes of Cu^{3+}, Ag^{2+} and Ag^{3+}, Ni^{+}, Cr^{5+}, Pt^{3+}, Pt^{5+}, Pt^{6+}, Pt^{8+}, have been shown[194-196] to exist with certain ligands. In these complexes, the donor–acceptor properties of the metal atom can differ very substantially from those of the same atom in its usual valency states. Several instances of catalytic activity have been reported for metals in unusual oxidation states. Rich and Taube[197] showed that a number of isotope exchange reactions are catalysed by Pt^{2+} and Au^{2+} compounds. It has been pointed out[198] that Cr^{5+} ions are the active centres of chromium oxide polymerisation catalysts.

Once it is established that a particular oxidation state of a metal shows maximum catalytic activity, the factors which contribute to the stabilisation of this state can be evaluated. Ligands tending to form dative π-bonds stabilise the lower oxidation states[24]. The effect of the nature of the ligands on the stability of the states of a metal ion with a different number of d-electrons can easily be evaluated in the crystal field theory approximation. For example, the Cr^{5+} state, in which the ion has one d-electron, is stabilised by the ligand field. Cr^{6+}, on the other hand, has no d-electrons, and the stabilisation energy for this state is zero. Hence, the stability of the Cr^{5+} state increases with the strength of the ligand field.

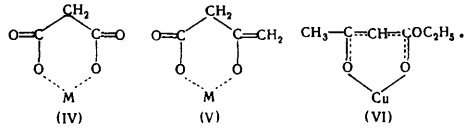
In all probability, the ligands themselves often participate directly in the catalytic process. Taube[199-201] believes electron transfer through a ligand bridge to be a possibility in oxidation–reduction reactions, and Stranks[195] considers this to be the most likely mechanism for the Cr^{2+}–Cr^{3+} system. Matveev and coworkers[133] believe that the oxidation of the Pd^0 complex by the Cu^{2+} ion during the catalytic oxidation of ethylene to acetaldehyde occurs through a bridging complex, and that electron transfer from ion to ion is accompanied by the transfer of a ligand. They point out that the oxidation is fastest when the ligand being transferred has an unshared electron pair.

Coordinated ligands can form hydrogen bonds with other molecules[74]. This effect can be important in controlling the orientation of reacting molecules, particularly in enzyme catalysis[32].

IV. COORDINATION INTERACTION AND CHARACTERISTICS OF THE TRANSITION STATE OF CATALYTIC REACTIONS

Several attempts have been made to use complexes as models of the transition state. Hammond[202] formulated the following postulate: if the transition state and the intermediate complex are formed consecutively during the reaction and have similar energies, their molecular structures can be expected to be similar. Since complex formation is an exothermic process, the postulate implies that the transition state and the intermediate complex can have similar structures only when the activation energy of the reaction is low.

The parallelism between the reaction rate and the stability of complexes is often interpreted as evidence for a similarity in structure between the complex and the transition state. Prue and Hoppe[95,203] suggested that the catalytic activity of metal cations towards the decarboxylation of acetonedicarboxylic acid and the hydrolysis of dicarboxylic acid and aminoacid esters depends on the mode of chelation of the activated complex in these reactions. They based this conclusion on the good correlation between the activity of various metal cations and the stability constant of the complexes of these metals with malonic acid. The structure of these complexes and the proposed configuration of the transition state for the decarboxylation of acetonedicarboxylic acid is shown by formulae (IV) and (V):



(IV) (V) (VI)

According to Bell[204], the transition state during the bromination of ethyl acetoacetate in the presence of copper ions is stabilised by a metal cation in a form similar to that of the chelate complex (VI).

The crystal field theory has made possible a new approach to the characterisation of the transition state. Several papers[7,18,23,24,205,206] have dealt with the activation energy of ligand replacement reactions in complexes. The transition state was treated as a complex in which the number of ligands per reacting unit is smaller (S_N1 mechanism) or greater (S_N2 mechanism) than in the starting complex. By assuming a specific steric configuration for the activated complex it is possible to estimate the change in the crystal field stabilisation energy attending the change from the starting complex to the activated complex. The result is one of the terms which make up the activation energy. tion energy.

The same approach can be applied to catalytic reactions. Dowden and Wells[207] applied the crystal field theory in their analysis of the catalytic activity of various metals, oxides, and sulphides. Unsaturated valencies on the surface of the catalyst were treated as empty sites in the coordination sphere of a complex having one of the surface cations as its central ion. A change in the coordination of the surface complex takes place during formation of the transition state of the limiting step, which includes adsorption. For example, a square pyramid changes to an octahedron, and a tetrahedron changes to a square pyramid. Under these conditions, the stabilisation energy due to the crystal field of the transition state will differ for the various catalysts according to the number of d-electrons in the metal. In this way, the authors were able to explain why the minimum activity in H_2–D_2 exchange reactions and in some

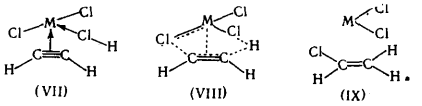
oxidation–reduction reactions is found with catalysts containing cations with d^0, d^5, and d^{10} electronic configurations, for which the stabilisation energy is zero. At the same time, the d^3 and d^7 systems (in which the stabilisation energy attending the formation of the activated complex is greatest) showed the maximum catalytic activity.

Krylov[208] points out that the opposite relationship should be observed when formation of the transition state involves a decrease rather than an increase in the coordination number. In this case the stabilisation energy due to the crystal field will decrease, as a rule, on formation of the transition state, and the highest catalytic activity will be found in d^0, d^5, and d^{10} systems. Catalysts of this type have been shown to be the most active in the polymerisation of ethylene oxide on metal oxides and hydroxides, in the dehydration of formic acid, etc.

Glasstone, Laidler, and Eyring[209] state that the transition state of many reactions can be expected to be similar to the final state. Hence, and in view of the important role of mixed complexes in catalysis discussed above, we may conclude that the transition state of many bimolecular reactions of the type

$$A + B \xrightarrow{K} \text{reaction products}$$

has a configuration intermediate between the final state and the mixed complex AKB. For example, the hydrochlorination of acetylene on MCl_2 salts[47] has been described by the following formulae for the mixed complex (VII), the proposed activated complex (VIII), and the final state (IX):



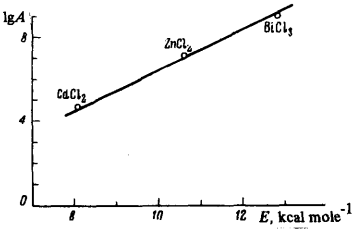


Figure 2. Compensation effect in the catalytic hydrochlorination of acetylene.

Structures (VII) and (VIII) can serve as an illustration of the present writers' suggestion[12,51] that the interaction between the catalyst and the reagent in the transition state can be similar to the interaction between the metal and the ligand in the corresponding complex. This hypothesis allows us to characterise the transition state in terms of data on the influence of CTI on the ligands, and to establish a relationship between the parameters of the metal ion which are important in coordination and the characteristics of the transition state of a reaction catalysed by the same ion. For the reaction

$$MCl_n \cdot C_2H_2 + HCl \rightarrow CH_2{=}CHCl + MCl_n \cdot$$

we had previously determined[47] the pre-exponential factor (A) and the activation energy (E). We found that both A and E increase along the series of catalytic salts $HgCl_2$–$CdCl_2$–$ZnCl_2$–$BiCl_3$, in which the acceptor properties of the cation increase and the donor properties decrease[12,49,51]. The relationship between lg A and E is accurately linear for the chlorides of Cd, Zn, and Bi (Fig. 2). Similar results were obtained for the catalytic synthesis of vinyl acetate from acetylene and acetic acid[48], and for the hydrochlorination of methanol[98]. Thus, at least some reactions show a definite relationship between the Arrhenius parameters and the donor–acceptor properties of the catalyst. This dependence may sometimes give rise to a compensation effect, since an increase in acceptor properties along a series of similar catalysts is usually accompanied by a decrease in donor properties. The decrease in activation energy accompanying an increase in the donor tendency of a catalyst can be explained by the drastic loosening effect of dative interaction on the reactant molecule[12,41–43,49,51,177,210].

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Karpov Physicochemical Institute
Moscow

*This may well be a reference to "Die organischen Katalysatoren und ihre Beziehungen zu den Fermenten", Berlin, Springer Verlag, 1949.

**[The author probably has in mind p. 398 of this reference (Ed. of Translation)].

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The Chemistry and Physicochemical Features of the Microbiological Oxidation of Petroleum Hydrocarbons

V.I.Karban, R.V.Kucher, and N.I.Mironenko

The review examines Soviet and foreign literature on the microbiological synthesis of proteins from petroleum hydrocarbons. The general characteristics of the process and the conditions for its occurrence are described together with the chemical mechanism of the microbiological oxidation of aliphatic, aromatic, and heterocyclic hydrocarbons. Particular attention has been devoted to the physicochemical and topochemical features of the process. It has been shown that the process is similar from the physicochemical standpoint to the oxidation of hydrocarbons in emulsions. The bibliography includes 241 references.

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I. INTRODUCTION

The enzymic synthesis of proteins and vitamins in the yeast cell has been attracting recently an increasing amount of attention from workers in many fields. A new branch of industry, dealing with the microbiological manufacture of amino-acids, vitamins, and other valuable products, has arisen and has been developing vigorously. Certain micro-organisms are known to be capable of utilising pure hydrocarbons[1-5], alcohols, and acids[6-9], and also petroleum and petroleum products[10-16] as sources of carbon and energy. The possibility of the oxidation of petroleum hydrocarbons by micro-organisms was pointed out as early as the 1920's–1930's by the leading Soviet microbiologist Tauson[17]. Certain species of micro-organisms develop very successfully in stagnant waters in petroleum-processing factories[18], in subsurface waters in petroleum deposits, in soils impregnated with petroleum[19], and also under bituminous road surfaces[20,21]. These micro-organisms are mainly aerobic and they metabolise saturated hydrocarbons, mainly with straight-chain structures[22,23]. Since the microbes are living organisms, they have a fairly rich protein store. Thus petroleum can become a source of proteins, which are an essential and the most deficient component in the food of man and animals.

According to McFerson's data[24], to make good this deficit, which is acute as far as the bulk of the world population is concerned, it will be necessary to produce in 1980 an additional amount of about 18 million tons of fats, 9.9 million tons of animal protein, and 11.4 million tons of amino-acids per year. The most convenient and cheapest of the principal raw materials for the synthesis of food products is petroleum and atmospheric nitrogen fixed in the form of ammonia.

The microbiological synthesis of food products is very convenient because of the high rate of multiplication of micro-organisms, their high biochemical activity, the possibility of using relatively cheap starting materials, and also the independence of the manufacture of climatic and weather conditions. Thanks to the progress in the technology of the growing of micro-organisms, favourable conditions have been created for the control of their development under industrial conditions.

At the present time there exists a fairly extensive Soviet and foreign scientific literature on the development of micro-organisms on separate fractions of petroleum and on pure hydrocarbons[25-32]. In particular, one should mention the work of French investigators led by Champagnat[33-37]. By growing micro-organisms (mainly yeasts) on various petroleum fractions, they obtained proteins and valuable water-soluble vitamins. The product was called the protein-vitamin concentrate (PVC). At the same time the removal of paraffins improved the quality of the petroleum, since the solidification temperatures of the fuels and oils obtained from it are thereby reduced[38]. The work of Senez and coworkers[39-42] is of great interest in this respect. Recently extensive studies are being carried out in the USSR on the isolation and selection of micro-organisms assimilating petroleum hydrocarbons, experimental industrial apparatus for the manufacture of PVC has been set up, and tests are being made on the nutritional value and the possible harmful effects of the product[43-54].

The microbiological synthesis of proteins and vitamins from petroleum is based on the enzymic oxidation of hydrocarbons and their derivatives. Little is known at present about the conditions of the occurrence, mechanism, and products of microbiological oxidation, which differs appreciably from the chemical oxidation of these hydrocarbons, and the available information is not systematic and requires revision. Chemists, in close collaboration with microbiologists, biochemists, and workers in other fields, should play the main part in the creation of a theory of the enzymic oxidation of hydrocarbons.

II. GENERAL CHARACTERISTICS OF THE MICROBIOLOGICAL SYNTHESIS OF PROTEINS FROM HYDROCARBONS

The principal raw material for the manufacture of the protein–vitamin concentrate are liquid saturated petroleum hydrocarbons with a straight-chain structure obtained in the process of elimination of paraffins from Diesel fuels with subsequent purification by adsorption. Saturated hydrocarbons obtained in the low-temperature elimination of paraffins and purified with sulphuric acid are also suitable. As a result of such purification, the saturated hydrocarbons contain not more than 0.5% of aromatic

hydrocarbons. Certain species of micro-organisms can be grown on individual fractions of Diesel fuels without preliminary isolation of straight-chain saturated hydrocarbons from the latter. Then the paraffin-free part of the fuel must be separated from the crude protein mass.

In petroleum from different deposits the content of alkanes with different carbon chain lengths varies within wide limits. Different micro-organisms assimulate mainly saturated hydrocarbons with 10–24 (C_{10}–C_{24}) [1-5] and also 1–4 (C_1–C_4) [25-32,49] carbon atoms. Thus in most cases yeasts assimilate hydrocarbons ranging from n-nonane to n-octadecane (C_9–C_{18}) and also unsaturated hydrocarbons with the same carbon chain length[50].

Experiments show that micro-organisms exhibit definite selectivity in their capacity to assimilate a particular substrate[51-65]. Isoalkanes are utilised by micro-organism less satisfactorily than straight-chain alkanes[66]. Aromatic compounds are not very suitable as sources of carbon for micro-organisms of the genus Candida[56,67,68]. An even narrower substrate specificity has also been observed. Micro-organisms can grow on one hydrocarbon but not on another with a similar structure[69].

At the present time search is going on for highly active micro-organism cultures (mainly yeasts) ensuring rapid accumulation of biological material. Most investigators have devoted particular attention to yeasts of the genus Candida, since these are the most active[3,29,70].

Yeasts are rich in B vitamins, the content of which depends on the yeast culture, the nutritional medium, and the method of cultivation (Table 2), [47,48,89,90]. Yeasts grown on petroleum hydrocarbons contain vitamins combined with other growth factors of unknown composition.

Table 2. Content (mg) of water-soluble vitamins and their importance[30].

	Thiamine B_1	Riboflavine B_2	Nicotinic acid PP	Pantothenic acid	Pyridoxine B_6
Daily requirement in man	2	3	15	3	2
Content of vitamins in various products:					
Meat (beef)	1—3	2	40—100	7—21	1—4
Liver	5—10	16	75—275	30—60	5
Milk	0.3—0.7	1—3	1—5	1—4	1—3
Grain	0.5—7.0	1—1.5	10—30	5—20	3—6
Dry yeast	2—20	30—60	200—500	30—200	40—50
Protein-vitamin concentrate	3—16	75	130—200	150—192	23
Functions	carbohydrate metabolism	dehydrogenation, oxidation	carbon transport	acetylation. synthesis of aliphatic acids	transamination
Consequences of vitamin deficiency	nervous disorder, beri-beri	arrest of development	pellagra	arrest of development	dermatitis

Table 1. Content of certain amino-acids in yeast, meat, and wheat grain[30].

Amino-acid	Daily requirement in man, g	Amino-acid content, g/100g		
		in yeast	in animal tissues	in wheat grain
Arginine	3.5	4.3	7.1	3.0
Histidine	2.0	2.8	2.2	1.2
Lysine	5.2	6.4	8.1	2.7
Tyrosine	3.9	4.2	3.1	—
Tryptophan	1.1	1.4	1.2	1.0
Phenylalanine	4.4	4.1	4.5	9.3
Cystine + Methionine	3.8	1.3 traces	1.1 + 3.3	with tyrosine 4.3
Leucine	9.1	13.2	12.1	13.0
Isoleucine	3.3	3.4	3.4	4.0
Valine	3.8	4.4	3.4	3.5
Threonine	3.5	5.0	5.2	3.3

The nutritional value of yeast was first pointed out by Dellbrook in 1875; this hypothesis was developed in later studies by other workers[71-78]. The nutritional value of protein is determined in the first place by the relative amounts of its constituent amino-acids[79]. The amino-acid composition of yeast protein depends on the yeast species, the nutritional medium, and the method of cultivating the yeast[80,81]. However, different yeast species do not show sharp differences in their amino-acid content[82] and this is the reason for the high biological value of yeast protein[83,84] (Table 1).

Yeast proteins are assimilated by [animal] organisms to the extent of 85–88%; in this respect they occupy an intermediate position between proteins of plant (65–75%) and animal (90–95%) origin[85-87]. Because of their high lysine and valine content, yeasts are a useful additive to cereal proteins and improves their nutritional value[88].

Like any other living organism, yeasts can exist only in the presence of water. Their nutrient must contain carbon, nitrogen, phosphorus, potassium, magnesium, and many micro-elements. Petroleum hydrocarbons are the exclusive source of carbon and energy. Nitrogen, phosphorus, potassium, and magnesium form part of the nutrient medium in the form of a solution of mineral salts in water. Thus microbiological oxidation takes place in an emulsion of the hydrocarbon in the aqueous phase. The elements essential for the growth and development of yeast include in the first place iron, zinc, and manganese[91,92]. Iron enters into the composition of many enzymes and is necessary for the growth of yeasts and the accumulation of biological material[93,94]. Zinc also enters into the composition of carboxyoxidase, cytochrome, cytochrome oxidase, and certain other enzymes[95]. Manganese influences the catalytic activity of many oxidative enzymes. One may assume that other elements, required in smaller doses, such as copper, molybdenum, cobalt, iodine, boron, and others, are present in sufficient amount in tap water and in the mineral salts usually employed in the cultivation of yeasts.

The principal parameter of process development is temperature. For each micro-organism there exists an optimum temperature at which the time required for cell division is a minimum. All these temperatures lie in the range 25–40°C [42,96,97] and therefore the microbiological oxidation of petroleum hydrocarbons is energetically more favourable than chemical oxidation, which occurs at an adequate rate only at elevated temperatures.

An important factor in the cultivation of micro-organisms on hydrocarbon substrates under aerobic conditions is the supply of oxygen. Oxygen is required not only to synthesise the biological material itself, but also to oxidise the hydrocarbon and to satisfy the energy requirements of the metabolism of yeast cells. The overall

requirement of oxygen in the growing of yeasts on hydrocarbons is higher by a factor of 2–4 than on carbohydrate substrates, since in the latter case oxygen is required only to make good the energy expended on the growth and is not fixed by the cell[30]. The oxygen needed by the micro-organisms must be dissolved in the aqueous medium. The limiting cell growth is determined by the diffusion of atmospheric oxygen into the medium.

At the present time the efforts of scientists and engineers are directed towards the development of a theory and the improvement of apparatus for continuous microbiological oxidation of petroleum hydrocarbons[98-102]. The microbiological oxidation of petroleum hydrocarbons may be carried out in two ways: by growing micro-organisms to be used as such in the form of protein-vitamin concentrates or by extracting from the aqeuous medium the valuable products synthesised by the micro-organisms. The industrial methods for the microbiological synthesis of amino-acids and vitamins used in many countries are based on these properties of micro-organisms[103-110]. The micro-organism species which, after metabolising the carbon-containing substances secrete into the reaction medium predominantly one or other amino-acid, are of particular interest. Glutamic acid and lysine are at present manufactured in this way on an industrial scale from carbohydrates and plant raw material. Scientists in the laboratories of Japan, the USA, the Soviet Union, and other countries are working intensively on the development of methods for the biological synthesis of other amino-acids[111-120].

III. THE CHEMICAL MECHANISM OF THE MICROBIOLOGICAL OXIDATION OF HYDROCARBONS

Numerous experiments have shown that the mechanism of the oxidation of hydrocarbons by micro-organisms differs from that of chemical oxidation. It has been firmly established that in the liquid-phase oxidation of hydrocarbons the primary oxidation product is a hydroperoxide, subsequently responsible for the degenerate branching of the complex chain oxidation process. The main radical propagating the reaction chains is the peroxy-radical $ROO^{\cdot}$.

The chemical oxidation of hydrocarbons has been investigated in detail by Emanuel' and coworkers[121,122], who elucidated a number of its kinetic features and proposed the following oxidation mechanism:

$$RH + O_2 \rightarrow R^{\cdot} + HO_2$$
$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$$
$$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$$
$$ROOH \rightarrow RO^{\cdot} + O^{\cdot}H$$
$$2RO_2^{\cdot} \searrow$$
$$R^{\cdot} + RO_2^{\cdot} \rightarrow \text{chain termination.}$$
$$2R^{\cdot} \nearrow$$

The mechanism of the microbiological oxidation of hydrocarbons differs from that given above and has been much less studied.

The assimilation of hydrocarbons by micro-organisms depends on the following conditions: the penetration of the hydrocarbons into the cell, the capacity of micro-organisms to become adapted to the hydrocarbons, and finally the presence of enzymes necessary for the primary oxidation of the hydrocarbons[123,124]. The penetration of hydrocarbons into the cells of the micro-organisms, which largely determines the topochemistry of the reaction, is to a considerable extent associated with the physicochemical features of the process, which will be examined below.

The adaptation phenomenon, which probably takes place at the level of enzymic systems, is now attracting the attention of many investigators[125-135]. Micro-organisms assimilating hydrocarbons must be adapted to the nutrient medium, which under natural conditions undergoes considerable changes. Some micro-organisms, die, having failed to adapt to the new conditions. Others gradually become adapted, and begin to assimilate the new substrates[136].

The intrinsic oxidation process takes place with the aid of enzymes which lower the activation energy by 16–18 kcal $mole^{-1}$, while non-biological catalysts result in a lowering of activation energy by only 4–8 kcal $mole^{-1}$.[137] Both the prosthetic group and certain groups of the protein carrier forming part of the active centre of the enzyme take a direct part in catalysis[138]. It has been shown[139,140] that the configuration of molecules in certain enzymes changes appreciably in the course of interaction with the substrates. Evidently the catalytic groups are then arranged in the order necessary for enzyme action on the substrate[141-143].

In the formation of the enzyme–substrate complex bonds are polarised and this is the cause of the "strained configuration" of the complex. In a complex of this kind the bonds are stretched and weakened[140]. The binding of the substrate by the enzyme induces a change in the conformation of the protein base of the enzyme, and, conversely, under the influence of the enzyme the substrate molecules are distroted and activated. The coordinated action of two of several groups of the active enzyme centre involving the polarisation of definite bonds in the substrate constitutes the basis of the catalytic action of the enzyme[144,145]. The kinetics of enzyme action are described by the Michaelis equation or more complex equations, depending on the number of components in the active centres[146,147].

The data on the role and mechanism of the action of enzymes in the microbiological oxidation of hydrocarbons are inadequate. Only recently interesting studies on the participation of enzymes in these processes have begun to be published[129,132,133,135,148].

The primary step in microbiological oxidation is attack by oxygen on the hydrocarbon molecule. Unfortunately, so far there is no unanimous view in the literature concerning the site of the attack. Many investigators believe that the most likely pathway in the microbiological oxidation of straight-chain paraffins involves the oxidation of one of the terminal methyl groups to a carboxy-group via the intermediate formation of an alcohol and an aldehyde[149-154].

Using the tracer atom method, Stewart and coworkers[155] showed that molecular oxygen is incorporated in the hydrocarbon molecule, the primary oxidation product being a hydroperoxide:

$$R{-}CH_3 \xrightarrow{+{}^{18}O_2} R{-}CH_2{}^{18}O{}^{18}O \rightarrow R{-}CH_2{}^{18}O\,H \rightarrow R{-}C^{18}O\,OH.$$

The presence of a hydroperoxide in the metabolic products is indicated also by other workers[40,156,157]. The possibility of the formation of a hydroperoxide as an oxidation intermediate is confirmed by the fact that synthetic alkyl 1-hydroperoxides are oxidised by micrococci grown on hydrocarbon substrates[136].

The process mechanism described above is not as yet reliably established. Apart from the oxidation of the terminal atom in the straight-chain hydrocarbon, it is believed that the carbon atom in the α-position may be oxidised[158]. Then the formation of aliphatic acids takes place via secondary alcohols and alkyl methyl ketones:

$$R{-}CH_2{-}CH_3 \rightarrow R{-}CHOH{-}CH_3 \rightarrow R{-}CO{-}CH_3.$$

Foster explains the oxidation of the carbon atom in the α-position on the hypothesis that the free radicals within

the chain of the straight-chain hydrocarbon are in equilibrium[165]. Primary activation consists in the formation of a free n-alkyl radical at the terminal carbon atom. However, the hydrogen atom can migrate within the molecule and activate the adjacent carbon atom, i.e. the primary radical isomerises to a radical with the corresponding iso-structure. The initial stable products formed by this mechanism are ketones. These compounds are detected only in certain cultures, grown on saturated hydrocarbons[158-161], but the relative ease with which methyl ketones are assimilated by micro-organisms oxidising hydrocarbons suggests that these substances may behave as intermediates in the oxidation of straight-chain alkanes, particularly those with a short chain[158-162].

In the cultivation of various bacteria (*Pseudomonas aeruginosa*, *Achromobacter* sp., *Nocardia* sp., *Mycobacterium* sp.) on purified hydrocarbons with an even and odd number of carbon atoms (C_6 and C_7), Treccani et al. noted the formation of saturated aliphatic acids with unbranched chains[163-165]. Lower alkanes with an even and odd number of carbon atoms yield various oxidation products[69]. When n-hexane is used as a substrate, caproic, butyric, and acetic acids are formed, while with n-heptane the products are all the [straight-chain] aliphatic acids containing between 1 and 7 carbon atoms in the molecule. This investigation requires additional experimental confirmation. The assimilation of alkanes with an even number of carbon atoms is hindered by the presence in the reaction mass of acids with an odd number of carbon atoms. If, on the other hand, the cells assimilate a hydrocarbon with an odd number of carbon atoms the presence of any aliphatic acids in the reaction medium does not interfere with the reaction[165].

It has been established that *Pseudomonas methanica* converts gaseous hydrocarbons into oxidation products with the same number of carbon atoms as the initial hydrocarbons[166-169]. When ethane, propane, and n-butane were added, the products detected were respectively acetic acid and acetaldehyde, propionic acid and acetone, and butyric acid and 2-butanone. In the microbiological oxidation of methane the extracellular products formed are methanol, formaldehyde, formic acid, carbon dioxide, hydrogen, and polysaccharides[170].

In the oxidation of n-hexadecane the final product is cetyl palmitate[165-171]. The cetyl alcohol which esterifies palmitic acid is formed from n-hexadecyl hydroperoxide, which is probably the first intermediate in the oxidation of n-hexadecane. Micro-organisms grown on hexadecane readily oxidised this hydroperoxide. An ester is also formed when micro-organisms are grown on octa- and tetra-decane[172]. The alcoholic component of the ester has the same hydrocarbon skeleton as the alkane in the substrate. On this basis, one may say that the alcoholic component of the ester obtained from the hydrocarbon is formed directly from the alkane by the oxidation of the terminal carbon atom.

On the other hand, according to Treccani[69], the acid component of esters in all cases of bacterial oxidation of alkanes probably contains 16 carbon atoms regardless of the chain length of the straight-chain hydrocarbon used as the substrate.

Gololobov believes[136] that palmitic acid is not always the acid component of the esters. This is also the view of Kallio and Finnerty[173,174], who isolated two esters from the medium in which micrococci were grown with octadecane: octadecyl palmitate $CH_3(CH)_{14}COOCH_2(CH_2)_{16}CH_3$ and octadecyl stearate $CH_3(CH_2)_{16}COOCH_2(CH_2)_{16}CH_3$.

The acid component of octadecyl stearate is formed as a result of the oxidation of the terminal carbon atom in octadecane:

$$CH_3-(CH_2)_{15}-CH_2-CH_3 \rightarrow CH_3-(CH_2)_{15}-CH_2-CH_2OH \rightarrow CH_3-(CH_2)_{15}-CH_2-COOH.$$

In octadecyl palmitate the acid component contains 2 carbon atoms less than the hydrocarbon. The formation of palmitic acid may be explained by assuming the oxidation of the α-carbon atom in octadecane with formation of a secondary alcohol and then an alkyl methyl ketone, the latter being subsequently split by the following mechanism:

$$CH_3-(CH_2)_{15}-\overset{\alpha}{C}H_2-CH_3 \longrightarrow CH_3-(CH_2)_{15}-\underset{OH}{\overset{\alpha}{C}H}-CH_3 \longrightarrow$$

$$\rightarrow CH_3-(CH_2)_{14}-\overset{H}{\underset{2O}{CH}}-\overset{\alpha}{\underset{O}{C}}-CH_3 \longrightarrow CH_3-(CH_2)_{14}-COOH + CH_3COOH.$$

As stated above, in the microbiological oxidation of hydrocarbons direct binding of oxygen is observed[175,176]. Many investigators suggest that primary enzyme action on the hydrocarbon molecules is possible with direct participation of oxygen. This hypothesis has been proved[169] by the incorporation of oxygen-18 into cetyl palmitate.

The possibility of the microbiological decomposition of hydrocarbons under anaerobic conditions appears to be less likely[177,178], but recent communications describe the development of specific hydrocarbon-oxidising bacteria of the genus *Pseudomonas* on a mineral medium with petroleum under anaerobic conditions[179].

Thus the conversion of aliphatic hydrocarbons consist in the formation during the initial reaction period of saturated aliphatic acids with unbranched chains. Different workers have obtained not entirely consistent results concerning the further breakdown of the aliphatic acids. In the view of the majority[156,159], acids with an even number of carbon atoms break down by a mechanism involving β-oxidation to acetic acid. When the number of carbon atoms is odd, the acids can also undergo α-oxidation and be converted into acids with an even number of carbon atoms, which subsequently undergo only β-oxidation to propionic and acetic acids. Thus, according to Stadman[23], *Methanobacterium suboxydans* converts valeric acid by β-oxidation into propionic and acetic acids, while butyric and caproic acids are converted into acetic acid.

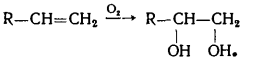
Certain bacterial species are capable of oxidising straight-chain alkane molecules from both ends, forming both mono- and di-carboxylic acids[180]. ω-Oxidation to dicarboxylic acids is evidently a secondary pathway and constitutes the first stages of the subsequent β-oxidation.

The oxidation of metabolic intermediates may be artificially retarded by adding to the reaction medium inhibitors such as sodium azide, sodium cyanide, $\alpha\alpha'$-dipyridyl, heavy metal ions, and others[23,181]. Possibly the use of inhibitors will prove useful in the investigation of the mechanism of the formation and accumulation of valuable products and also for the determination of the role of the enzymes involved in the process.

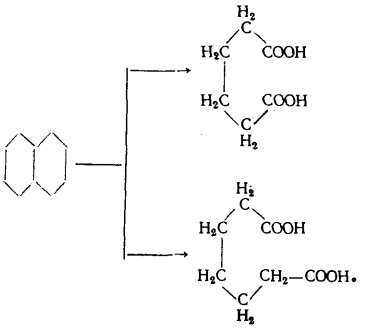
The mechanism of the bacterial oxidation of unsaturated compounds has been little investigated. It is known that micro-organisms are capable of assimilating olefins as sources of carbon and energy. According to Shturm's paper[182], unsaturated hydrocarbons are assimilated by micro-organisms more readily than the corresponding alkanes. Both saturated and double bonds in olefins are attacked. Thus van der Linden and coworkers established that in the decomposition of oct-1-ene by cells of *Pseudomonas aeruginosa* the principal changes take place at the

saturated end of the molecular chain of the olefin, while the double bond is not affected[183].

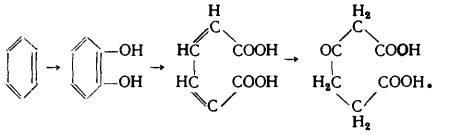
The finding that the oxidation of hexadec-1-ene by the yeast *Candida lipolytica* results in the accumulation of hexadecane-1,2-diol as an intermediate[184] is interesting. This indicates the possibility of the simultaneous oxidation in the olefin at the two carbon atoms linked by a double bond[185]:



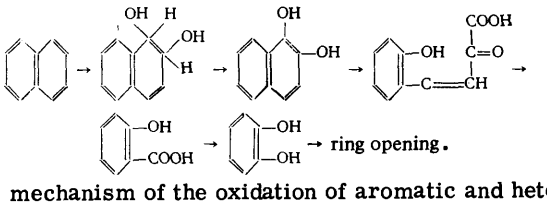
Little is known about the mechanism of the microbiological oxidation of cyclic saturated compounds such as cyclohexane, decalin, perhydrophenanthrene, and perhydroanthracene[186,187]. The formation of a peroxide formaldehyde, and valeric and formic acids when *Pseudomonas fluorescens* is grown on cyclohexane has been demonstrated. When *Flavobacterium* is grown on decalin, adipic acid is an intermediate[189]:



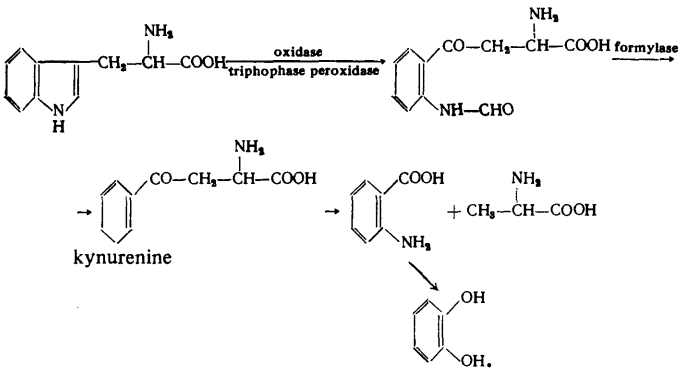
Micro-organisms assimilate aromatic compounds by converting them into *o*- or *p*-dihydroxy phenolic derivatives and then splitting the ring to aliphatic acids[190,191]. In the oxidation of benzene[192,193] catechol is formed as an intermediate; phenol and *cis,cis*-muconic acid also accumulate[194]. Benzene oxidase, which converts benzene into 3-oxoadipic acid, has been isolated from cells grown on benzene[195,196]. The enzymic extract does not contain phenol oxidase and only whole cells grown on phenol (but not adapted to benzene) immediately bind oxygen in the presence of phenol. The oxidation of benzene can be represented by the following mechanism:



Walker and Wiltshire showed in their investigation of the pathways for the decomposition of naphthalene during the growth of five different microorganisms that in all cases the intermediates are naphthalenediol, salicyclic acid, and catechol. The same mechanism has been confirmed by the work of Azoulay and coworkers[198,199]:



The mechanism of the oxidation of aromatic and heterocyclic hydrocarbons has been described in detail in Treccani's review[69]. For example, the decomposition of tryptophan takes place by the following mechanism:



Indole reacts similarly. The microbiological oxidation of indolylacetic and nicotinic acids, nicotine, aromatic nitrocompounds, and compounds of the lignin group have also been studied.

IV. PHYSICOCHEMICAL AND TOPOCHEMICAL FEATURES OF THE PROCESS

Brief examination of the chemistry of the oxidation of petroleum hydrocarbons convincingly demonstrates that only the first steps have been taken in its investigation. The available data are far from adequate.

At present no papers have been published on the physical chemistry of microbiological oxidation and the kinetics of its individual stages. However, in view of the current importance of this process and its application in industry such information is very necessary, since without the knowledge of the physical chemistry and kinetics of the process it is difficult to consider the possibility of its rational control.

It is stated in papers published recently that during the growth of yeast cells free radicals are observed[200,201]. This is confirmed by the presence of ESR signals in the yeast *Saccharomyces cervisiae* and also in the oxidation of NADH by the cells of *Mycobacterium phlei*. In the latter case it is suggested that the ESR signals may be due to radicals similar in structure to semiquinone. The possible participation of free radicals in microbiological oxidation may be established by studying the chemiluminescence arising when free radicals act upon yeast cells[202]. The considerable role of free radicals in enzymic oxidation processes has been confirmed by the work of Emanuel' and coworkers on enzymic oxidation involving succinate dehydrogenase and other enzymes[203-206]. Free radical reactions in enzymic oxidation may be inhibited by inhibitors of chain oxidation processes, such as phenolic compounds and others. All these findings show that one cannot exclude the possibility that individual stages in the microbiological oxidation of petroleum hydrocarbons take place with participation of free radicals.

The microbiological oxidation of petroleum hydrocarbons takes place in a complex system consisting of several phases. The hydrocarbon in a dispersed state and the cells of the micro-organisms are present in the aqueous medium. As a result of the growth of the micro-organisms, surface-active substances responsible for the additional emulsification of the hydrocarbon are produced[36,37]. All this suggests that the system is extremely

complicated. Factors associated with the vital activity of micro-organisms and also with the colloidal-chemical nature of the system are superimposed on the purely chemical processes. From this point of view, it is desirable to examine the mechanism of the penetration of the hydrocarbon into the cells present in the aqueous phases, since the process is impossible without the two component parts of the system coming into contact. There exist various theories explaining the mechanism of the entry of nutrient materials into the cell. Thus Johnson suggests[66] that the penetration of the hydrocarbon into the cell takes place with participation of the lipids in the cell membrane the long alkane chain becoming part of the phospholipid micelle of the cell membrane. This explanation is very general and it leaves many facts obscure. It has been suggested that the initial oxidation of the alkane takes place outside the cell[207]. Then it would be necessary for certain enzymes to be secreted by the cell into the medium[208], but many workers disagree with this postulate[136]. An interesting amount of evidence shows that the enzyme must be incorporated in definite structural formations within the cell in an unchanged form in order to exhibit its activity[209-217].

The intracellular activity of enzymes may be increased by surface-active emulsifying agents, as happens when such agents act upon the yeast *Candida albicans*[218]. In this case the catalase activity of *Candida albicans* increases by virtue of the increase in the permeability of the cell wall under the action of ionic surface-active substances. The interaction of surface-active emulsifying agents with *Saccharomyces ellipsoideus* leads to the formation of complexes with the lipids, lipoproteins, or proteins of the cell surface, whereby metabolic processes are distorted[219].

The complexity of the reaction system suggests that, in order to formulate the general laws governing the process, it is necessary to examine its topochemistry. Since virtually no such investigations of microbiological oxidation have been made, we believe it interesting to consider briefly the oxidation in emulsion of petroleum hydrocarbon, which resembles microbiological oxidation from the physicochemical standpoint. Probably later it will be possible to draw a number of analogies between the two reactions. The kinetics of the oxidation of hydrocarbons in emulsions have been thoroughly studied by Kucner and coworkers, who put forward a hypothesis concerning the topochemistry of the process[220-222].

In the first place they showed that surface-active emulsifying agents constitute an important kinetic factor; they alter the rate of the process (usually increase it) as a result of the stabilisation of the hydrocarbon droplets and also the droplets of the reaction products in the aqueous medium.

When hydrocarbons are oxidised in emulsions, it is quite possible that individual stages of the process take place in the aqueous phase[222]. By postulating the existence of micelles of the emulsifying agents, the nucleus of which consists of the organic part of the molecule and is oleophilic, one may assume that water-insoluble substances will dissolve fairly readily in the nucleus of the micelle. As a result, the loose micellar structure, which is constantly in contact with water, contains a high local concentration of the reactants which are subject to the polarising action of water. Here it is quite reasonable to assume an enhanced reactivity of the solubilised substances.

In this case the hydrocarbon phase is a source of the reactants which undergo solubilisation. Furthermore, the reaction products formed in the aqueous phase diffuse into the hydrocarbon phase. It is quite reasonable that all these processes should be coupled with the diffusion of the reactants from one phase to the other. A somewhat simplified topochemical mechanism of the reaction is presented in Fig. 1.

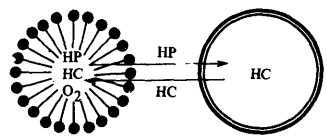


Figure 1. Topochemical mechanism of the oxidation of hydrocarbons in emulsions in the presence of an emulsifying agent. [HP (hydroperoxide) and HC (hydrocarbon) are the tentative interpretation of the Russian abbreviations GP and UVC (Ed. of Translation).]

However, this mechanism is not universal. It postulates the presence of surface-active emulsifying agents in the system and completely disregards the oxidation of hydrocarbons in emulsions not stabilised by such agents.

A number of experiments[223] convincingly demonstrate that the pressure of oxidising oxygen plays a significant role in the oxidation of hydrocarbons in emulsions. Thus in the oxidation of isopropylbenzene in a stainless steel autoclave an increase of pressure up to 10 atm leads to an increase of the reaction rate, which, however, scarcely changes any more when the pressure is raised above 15 atm. All these findings suggest that the oxidation of hydrocarbons in emulsions at atmospheric pressure is diffusion-dependent and is not determined by the kinetics. Then the rate of the process is limited by the solubility of oxygen in the emulsion and particularly in the aqueous phase. It has also been established[224] that the solubility of oxygen in the aqueous phase increases appreciably in the presence of dissolved surface-active emulsifying agents. Fig. 2 shows that the solubility and particularly the rate of dissolution of oxygen are higher in solutions of emulsifying agents than in pure water.

Finally, it has been established by a number of kinetic experiments on the oxidation of hydrocarbons in emulsions that the individual stages of the reaction (in this case it is the initiation reaction, taking place in the decomposition of a hydroperoxide) occur at the interface[225]. In particular, this applies to reactions in which surface-active agents (for example hydroperoxides), which are adsorbed on the surface of hydrocarbon droplets, take part. Here different media act upon different parts of the reactant molecule. The organic (hydrophobic) part of the molecule is drawn into the hydrocarbon medium, while the hydrophilic part is solvated by water molecules.

Thus the difference between the chemical potentials of the substance, different parts of the molecule of which are in different phases, gives rise to an additional polarising effect, which leads to an enhanced reactivity of the reactant. This is particularly evident in the decomposition of the hydroperoxide, the rate of which increases appreciably in the presence of the aqueous phase (Fig. 3).

Turning back now to the consideration of the microbiological oxidation of hydrocarbons, we may note the similarity of a number of its features with the oxidation of hydrocarbons in emulsions. In the first place the individual stages of the reaction take place in different phases or at the interface. The cell membrane consists of diphilic protein molecules, the structure of which resembles the diphilic structure of the molecules of surface-active emulsifying agents[226]. In this case the incorporation of the hydrocarbon between the organic chains of the hydrophobic "tails" of the protein molecules, similar to that occurring in the solubilisation of oleophilic substances in the so called "lamellar" micelles, is quite likely[227].

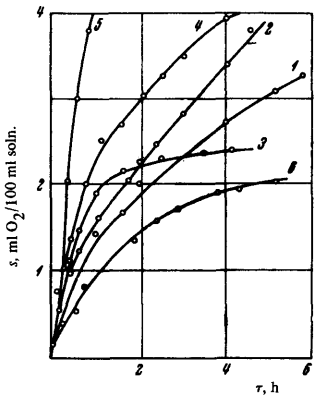


Figure 2. Kinetics of the dissolution of oxygen: 1) in 5% solution of Nekal; 2) in 5% solution of Leukanol; 3) in 0.1 *N* solution of potassium palmitate in 0.1 *N* solution of sodium carbonate; 4) ditto with solubilised isopropylbenzene; 5) in isopropylbenzene at 80°C; 6) in 0.1 *N* solution of sodium carbonate at 25°C.

Probably exceptionally favourable conditions are achieved at the interface, and in the first place on the surface of the cell, for the formation of the enzyme–substrate complex, since in this case a very high local concentration of these species is set up. The rate and kinetics of microbiological oxidation should also be influenced by the degree of dispersion of the reactants. This applies both to the degree of dispersion of the hydrocarbons droplets and the bubbles of the oxidising gas. These questions require systematic investigation. In their solution it is necessary to carry out experiments showing to what extent the rate of the process changes during the mechanical stirring of the reaction mixture. The study of the effect of the mechanical stirring of the oxidising emulsion of the hydrocarbon should make it easier to elucidate the role of diffusion factors in the kinetics of the microbiological oxidation of hydrocarbons, since an increase in the stirring rate produces an increased rate of diffusion of the individual components.

It is quite likely that, when the reaction is carried out at atmospheric pressure, the topochemical mechanism quoted above (Fig. 1) may be used for its explanation to some extent. In this connection it is also interesting to elucidate the effect of the solubilisation of the individual components in the aqueous phase on the process kinetics. We believe that such studies should be performed under conditions of a continually decreasing amount of the hydrocarbon phase until the complete disappearance of the hydrocarbon–aqueous solution interface.

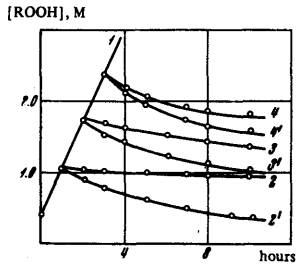


Figure 3. Kinetic curves for the oxidation of isopropylbenzene in emulsion (curve *1*) and for the breakdown of the hydroperoxide in the separated hydrocarbon phase (curves *2*–*4*) and in the emulsion (curves *2′*–*4′*) at 110°C.

Finally, the last process requiring solution at the present time is the effect of the increasing pressure of the oxidising gas containing oxygen. At an elevated pressure the solubility of oxygen increases. Thus, when the concentration of oxygen in the aqueous phase is raised, the rate of its diffusion into the hydrocarbon droplets or cells saturated by the hydrocarbon also rises. Then the process may be accelerated, as is observed in the oxidation of hydrocarbons in emulsions, but in microbiological oxidation account must be taken of the effect of pressure on the metabolism of the micro-organisms[228]. It is known from the literature that high pressures (up to 200 atm) are destructive to yeast organisms[70]. At a pressure in excess of atmospheric, oxygen may suppress and limit the growth of micro-organisms capable of developing in various nutrient media. Further studies should be directed towards the search for cultures stable under conditions of increased oxygen pressure.

From the kinetic standpoint, microbiological synthesis of proteins (more correctly its individual stages) takes place in an open system, since there is material exchange between the reaction site and the external medium[229]. A change in the amount of substance in an open system results not only from chemical processes but also from material exchange with the surrounding medium, which must be taken into account in the determination of the reaction rate.

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The aim of the present review was to examine the present state of our knowledge of the mechanism of the microbiological oxidation of petroleum hydrocarbons. The importance of this problem is evident. The interest which it has aroused has led to what is actually a new branch of natural science, at the boundary between chemistry and microbiology, which deals with the problems of the preparation of various substances with the aid of micro-organisms. Although microbiological synthesis itself has been known and used industrially for a long time, insufficient

attention has been devoted so far to the processing by this procedure of petroleum hydrocarbons, despite its importance. This applies to the physicochemical features of the process, since its microbiological and biochemical aspects have been vigorously investigated. To avoid overloading the review, many important purely biochemical and microbiological problems, which have been dealt with in other reviews, are omitted.

Much attention was devoted to the biosynthesis of proteins and vitamins at the Eighth and Ninth International Microbiological Congresses held in recent years (Moscow, 1962 and 1966), the Conference on Applied Microbiology, (Stockholm, 1963), the Symposium on Petroleum Microbiology (Czechoslovakia, 1964), and other scientific meetings[230-233]. At the present time most of the work in the field of microbiological synthesis concerns the accumulation of experimental data on the selection of the raw material and the micro-organism cultures, the study and isolation of the oxidation products, the development of methods for the control and investigation of the process, and also the relevant apparatus. Process conditions are selected and the nutritional value of the oxidation product is studied. Some advances have been made in the establishment of the mechanism of the enzymic oxidation of hydrocarbons and the role of trace elements in this process, and the mechanism of the interaction of the living cell with the hydrocarbon is being studied.

However, we believe that the time has come for a more detailed investigation of the chemical (particularly physicochemical) aspect of the microbiological oxidation of hydrocarbons. As in all developing branches of science, there are a number of factors here concerning which there exist only reasonable guesses or the data are contradictory. There has been hardly any work on the physicochemical aspect of the process, although such studies are of primary importance for the improvement of the technology. The chemists studying this process should employ the available literature data on similar processes (liquid-phase oxidation of hydrocarbons, reactions in emulsions, etc.).

The main difficulty in the investigation of the enzymic oxidation of hydrocarbons is in the first place the complexity of the reaction system, which requires the combined efforts of investigators in many fields, including many branches of chemistry. The weak development of our knowledge concerning the purely chemical aspect of enzymic processes, particularly as regards the microbiological oxidation of hydrocarbons, also hinders studies in this field. The development of such investigations promises to create a new technology of the preparation of food products and animal feed and also the synthesis of valuable organic substances (amino-acids, vitamins, etc). There is reason to believe that the development of the theory, the elucidation of the general laws governing the microbiological oxidation of hydrocarbons, and in particular the chemical mechanism of the process, will advance significantly in the next few years. It is quite clear that the extension and deepening of knowledge concerning the mechanism of the enzymic oxidation of petroleum hydrocarbons will lead to a real improvement of the existing technological processes for the synthesis of proteins from petroleum and also the organisation of new processes involving the selective conversion of petroleum hydrocarbons into important products and intermediates in industrial organic synthesis.

During the preparation of this review for the press, new papers on the enzymic oxidation of solid straight chain alkanes by different groups of micro-organisms were published[234,235]. The unsatisfactory growth of certain hydrocarbon-oxidising micro-organisms on solid alkanes can be explained in many cases by the instability of the dispersions of these hydrocarbons. Even in the presence of emulsifying agents, comminuted solid alkanes form large particles in an aqueous medium, which hinders the growth of micro-organisms. Miller and Johnson[234] suggest that solid alkanes be dissolved in liquid hydrocarbons which are not themselves assimilated by a given micro-organisms (or are assimilated to only a slight extent) and can serve as solvents. These workers grew *Candida intermedia* and *Candida lipolytica* on eicosane (C_{20}) and hexadecane (C_{16}) dissolved in pristane (2,6,10,14-tetramethylpentadecane) and noted a high yield of cells. However, the number of alkanes which can be investigated under these conditions is limited by their solubility in pristane.

Recently papers have also been published on the action of surface-active substances on micro-organisms and the study of the relation between the structure and functions of surface-active substances[236,237]. These investigations show that surface-active materials react with the cell wall, altering its permeability and giving rise to a loss of metabolically important components of protoplasm (various amino-acids and nucleic acid derivatives) as a result of the breakdown of osmotic equilibrium. Surface-active substances also influence the localisation of enzymes within the organism and the interaction between the enzymes. Depending on the pH of the medium, there is either an increase in the activity of enzymes in the presence of surface-active materials or their catalytic effect is suppressed.

As before, much attention is devoted to problems of the microbiological conversion of aromatic hydrocarbons[238,239] and also the growth of micro-organisms on gaseous hydrocarbons[240,241].

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Donets State University
Donets Division of the
Institute of Physical-Organic
Chemistry of the Academy
of Sciences of the Ukrainian
SSR

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Homogeneous Hydrogenation

M.E.Vol'pin and I.S.Kolomnikov

The present review examines catalytic systems which activate molecular hydrogen. Particular attention is paid to catalysis by compounds of transition metals. These systems are discussed in the following order: catalysis by salts of transition metals; catalysis by salts of transition metals in the presence of reducing agents (complex-forming reagents); and catalysis by individual complexes. General problems relating to the activation of hydrogen and the mechanism of the hydrogenation of organic compounds are also discussed. A separate section is devoted to the activation of molecular hydrogen by enzymatic systems. The bibliography contains 282 references.

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I. INTRODUCTION

Increasing attention is now being paid to homogeneous reactions involving complexes of transition metals: hydrogenation, hydroformylation, the polymerisation and oxidation of alkenes, the fixation of nitrogen, etc. A number of factors, for example the mode of activation of the substrate, the nature of the active species, etc., are common to these processes. Many hydroformylation catalysts are also effective hydrogenation catalysts; various Ziegler–Natta polymerisation catalysts are also active catalysts for hydrogenation and the fixation of nitrogen, etc. The investigation of the systematic features of these processes is therefore of general importance.

The problem of homogeneous hydrogenation is also of practical interest. For example, the use of molecular hydrogen in the polymerisation of alkenes by means of Ziegler–Natta catalysts makes it possible to control the molecular weight of the polymers formed[1], and homogeneous hydrogenation catalysts are used in fuel cells[2].

Research workers have long recognised the advantages of homogeneous over heterogeneous catalytic hydrogenation; the most important advantages are the ease of regeneration of the catalyst and the milder conditions of the process, combined with high efficiency, selectivity, and stereospecificity, and convenience for kinetic studies. In the last ten years the number of known homogeneous hydrogenation catalysts has increased considerably, and this has made possible a deeper and more complete study of a number of problems relating to the mechanism of hydrogenation.

In general, homogeneous hydrogenation with the participation of molecular hydrogen involves two inter-related stages: 1) the activation of molecular hydrogen; and 2) the actual hydrogenation, including activation of the substrate and the transfer of activated hydrogen to the substrate.

In the activation stage, molecular hydrogen reacts with the active compound with rupture of the H–H bond and the eventual formation of a hydrido complex, which may undergo further reactions (isotopic exchange, hydrogenation, etc.). Proof of the intermediate formation of these hydrides is an important task in the study of the mechanism of hydrogenation.

The activation of hydrogen has been the subject of an extensive review by Halpern[3], various papers[4–10], and individual chapters in other reviews[11–13]. The amount of work in this field has increased considerably since then, and the number of known homogeneous hydrogenation catalysts has increased significantly.

The present review covers data published up to 1967 and part of the data published in 1968; particular attention has been paid to the latest developments in the study of the mechanism of the activation of molecular hydrogen and homogeneous hydrogenation. Catalytic systems are classified as follows: a) systems without transition metal compounds; b) systems with transition metal derivatives; and c) biological systems.

It seemed convenient to consider isotopic exchange and the ortho-para conversion of hydrogen separately from hydrogenation.

II. ISOTOPIC EXCHANGE AND CONVERSION OF HYDROGEN

The isotopic exchange of molecular hydrogen and the conversion of ortho-hydrogen into para-hydrogen, which unavoidably involve rupture of the H–H bond, can be used successfully to study the activation of hydrogen. A significant advantage of these reactions compared with hydrogenation is their convenience for kinetic studies and their relative simplicity, since there is no need for the activation of a substrate, and the chemical changes in the system are minimal. Comparison of the results of studies of the exchange and conversion of hydrogen with data on hydrogenation for the same catalytic system provides an extremely fruitful method for investigating the mechanism of the activation of hydrogen and hydrogenation.

1. ACID–BASE SYSTEMS

Available data indicate the possibility of heterolysis of the H–H bond, primarily under the influence of various bases.

As early as 1936, Witz and Bonhoeffer[14] established that a 1 *N* aqueous solution of alkali at 100°C catalyses the exchange of molecular hydrogen with D_2O. The catalysis of the exchange and conversion of hydrogen by bases in aqueous solutions was subsequently studied by various groups of workers[15–19].

The kinetic studies of Wilmarth and coworkers[16] and Shindewolf[19] showed that the rate-determining stage of the reaction is the activation of H_2O by one hydroxide ion. In alcoholic solutions, the RO^- anion may act as hydrogen activator[19,20].

The activation energy for rupture of the H–H bond depends to a marked extent on the basic nature of the catalyst. Thus for the KNH_2–NH_3 catalytic system[19,21–25] this energy is 15 kcal mole^{-1} lower, and for the sodium acetate–acetic acid system 10 kcal mole^{-1} higher, than that for the reaction in aqueous alkali solutions[19]. The lowest activation energy for rupture of the H–H bond was observed when C_2H_5NHK–$C_2H_5NH_2$, that is the least basic catalytic system, was used[20]. Dilute and concentrated acids[16,17], and the BF_3–HF system[6], do not catalyse the exchange and conversion of hydrogen.

2. SYSTEMS CONTAINING SALTS OF TRANSITION METALS

The homogeneous isotopic exchange and ortho-para conversion of hydrogen in the presence of salts of transition metals was first observed by Calvin[26]. To explain these results he assumed a scheme involving the intermediate formation of the transition metal hydride:

$$n\,Cu^{I} + H_2 \rightleftarrows Cu^{I}_n \cdot H_2$$
$$Cu^{I}_n \cdot H_2 + 2\,Cu^{II} \rightleftarrows (n+2)\,Cu^{I} + 2\,H^+$$

It was found that in the presence of Cu^{II} acetate, neither conversion nor isotopic exchange of hydrogen takes place, and the molecular hydrogen is used up only in the reduction of the bivalent copper acetate; it is only when this reaction is complete that the Cu^{I} acetate formed begins to catalyse the exchange and conversion of H_2. It has also been reported[27], however, that the competing reactions of reduction and the isotopic exchange (or conversion) of hydrogen take place simultaneously under these conditions.

The rate of the ortho-para conversion is greater than the rate of the isotopic exchange of hydrogen. This is due to the fact that the conversion of hydrogen generally involves the recombination of two hydrogen atoms on a single metallic centre, whereas the exchange of hydrogen also requires interaction between the metal–hydrogen bond and the solvent. The isotopic exchange and ortho-para conversion of hydrogen are catalysed not only by copper salts but also by salts of silver, ruthenium, cobalt, etc. Both heterolytic and homolytic rupture of the H–H bond may take place. Thus homolytic rupture of the bond in the hydrogen molecule apparently takes place when the $CoCl_2$–KCN catalytic system is used[19,28,29], and also in the presence of copper acetate in quinoline[30]. On the other hand, detailed study of the kinetics of the exchange and conversion of hydrogen in the presence of $RuCl_3$–HCl–H_2O [19,31,32] showed that the hydrogen in this system undergoes heterolytic splitting according to the scheme:

$$Ru^{III}Cl^- + D_2 \rightarrow Ru^{III}D^- + D^+ + Cl^-$$
$$Ru^{III}D^- \xrightarrow{HCl} Ru^{III}Cl^- + HD$$
$$Ru^{III}D^- \xrightarrow{H_2O} Ru^{III}H^- + HOD$$
$$Ru^{III}H^- \xrightarrow{HCl} Ru^{III}Cl^- + H_2$$

where $Ru^{III}Cl^-$ represents the active chloro-complex of ruthenium.

According to this scheme, the exchange and conversion of hydrogen are accompanied by the intermediate formation of hydride (and deuteride) complexes of ruthenium. Of particular interest in this connection are the recently prepared iridium complexes $IrHD(CO)(PPh_3)_3$, which contain H and D attached simultaneously to the same metal atom, and which are active in hydrogenation[33]. It may be assumed that the study of the properties of these mixed hydrides will make it possible not only to reach a deeper understanding of the individual stages in the exchange, but also to reach definite conclusions regarding the structures of the intermediate hydride complexes.

III. HYDROGENATION

1. SYSTEMS WITHOUT COMPOUNDS OF TRANSITION METALS

a. Hydrogenation Under Conditions of Acid-base Catalysis

Systems of basic character, capable of catalysing the isotopic exchange and ortho-para conversion of hydrogen, can be regarded as potential hydrogenation catalysts. Basic systems of this kind were first used for hydrogenation by Walling and Bolliki[34,35], who showed that in the presence of potassium t-butoxide in butanol, benzene, or diglyme under fairly severe conditions (170–200°C, H_2 pressure 90–140 atm), benzophenone is hydrogenated with the formation of benzhydrol. The authors cited consider that in this instance the hydrogen undergoes heterolytic splitting with the formation of a hydride ion, which takes part in the first stage of the hydrogenation:

$$RO^- + H_2 \rightleftarrows ROH + H^-$$
$$H^- + R_2C{=}O \rightleftarrows R_2CH{-}O^-$$
$$R_2CH{-}O^- + ROH \rightleftarrows R_2CHOH + RO^- .$$

Aniline could be obtained from nitrobenzene under the same conditions; an attempt to hydrogenate cyclohexene was unsuccessful, and an attempt to hydrogenate acetone led to an aldol condensation.

The same authors also studied the possibility of acid-catalysed hydrogenation with activation of the hydrogen by means of a carbonium ion:

$$R^+ + H_2 \rightleftarrows RH + H^+ .$$

Thus when Lewis acids were used to obtain the carbonium ion (16% solution of $AlBr_3$ in cyclohexane at 150°C and 82 atm H_2), appreciable absorption of hydrogen was observed. A small quantity of hydrogen was also absorbed by benzene in the presence of $AlBr_3$, but neither cyclohexane nor methylcyclopentane were detected in the reaction products. In the hydrogenation of 2-methylpropene and cyclohexene in the presence of $AlCl_3$ in $CHCl_3$ at 140°C and 120 atm H_2, traces of saturated hydrocarbons were detected.

Thus even if acid catalysis of hydrogenation is possible, it takes place with much greater difficulty than base catalysis.

b. Hydrogenation Catalysed by Systems Based on Compounds of Boron and Aluminium

Köster and coworkers[36,37] showed that homogeneous hydrogenation of alkenes takes place in the presence of alkylboranes at temperatures greater than 200°C and a hydrogen pressure of 70 atm. DeWitt and coworkers[38,39], using boranes as catalysts, hydrogenated cyclohexene, oct-1-ene, polymers of butadiene, etc. With the trialkyl derivatives of boron, the first stage of the reaction gives a hydride, which subsequently reacts with the substrate:

$$BR_3 + H_2 \rightleftarrows R_2BH + RH$$
$$R_2BH + RCH{=}CH_2 \rightleftarrows RCH_2CH_2BR_2$$
$$RCH_2CH_2BR_2 + 2H_2 \rightarrow RCH_2CH_3 + RH + RBH_2 .$$

The same authors also made a detailed study of the influence of added Lewis acids on the hydrogenating power of alkylboranes. Lewis acids catalyse the addition of boron hydrides to alkenes, but in the present instance it was found that Lewis acids do not lower the hydrogenation temperature. In the opinion of the authors cited, this shows that the rate-determining stage of the reaction is the hydrogenolysis of the B–C bond.

The use of aluminium hydrides as catalysts for homogeneous hydrogenation was described in the patent literature[40]. Recently, Slaugh[41] showed that $LiAlH_4$ may act as a selective catalyst for the homogeneous hydrogenation of conjugated dienes (cyclo-octa-1,3-diene, cyclopentadiene) and dialkylacetylenes (pent-2-yne) to monoalkenes (hydrogenation takes place above 150°C in an atmosphere of H_2). A reaction scheme involving the formation and subsequent hydrogenolysis of an Al–C bond was proposed:

$$CH_3{-}CH{=}CH{-}CH{=}CHCH_3 + LiAlH_4 \rightarrow LiAlH_3(n\text{-}C_5H_9) \xrightarrow{n\text{-}(C_5H_9)} LiAlH_3(n\text{-}C_5H_9)_2 \text{ etc.}$$
$$LiAlH_3(n\text{-}C_5H_9) \xrightarrow{H_2} n\text{-}C_5H_{10} + LiAlH_4$$

Tracer studies showed that the hydrogenation of a conjugated diene involves one hydrogen atom from the hydride and another from the gaseous phase.

2. SYSTEMS CONTAINING COMPOUNDS OF THE TRANSITION METALS

Calvin's work[26,42] laid the foundation for the study of an extensive branch of homogeneous catalysis—the activation of molecular hydrogen by salts of transition metals. These systems, of which the great majority have been studied by Halpern and his school, can activate hydrogen under mild conditions, and their study has played an important part in the development of the theory of the activation of hydrogen and homogeneous hydrogenation.

The activation of hydrogen by transition metal complexes has been the subject of recent successful studies. It is difficult to make a sharp distinction between these two types of catalyst. For example, a polarographic study[43] of solutions of univalent copper salts in pyridine showed that the solution contains the ionic complexes $CuPy_2^+$, $CuPy_3^+$, $CuPy_4^+$, and $CuPy_6^+$. The ligands may be negative ions (Cl^-, CH_3COO^-, etc.) or uncharged molecules (amines, water, etc.). For convenience in the subsequent discussion, however, we shall divide catalysts of homogeneous hydrogenation involving transition metal compounds into three classes: a) salts of transition metals (in this instance the reaction of the salts with the solvent leads to the formation of a complicated system of ionic complexes); b) two-component systems (in this instance the transition metal salt reacts with organometallic compounds or with complex-forming reagents); and c) individual transition metal complexes with known composition.

a. Salts of Transition Metals

The catalytic activity of solutions of transition metal salts in water and in ammonia has been most widely studied. Reactions of three types have been studied: 1) the exchange and conversion of hydrogen, examined above; 2) the reduction of inorganic ions ($Cr_2O_7^{2-}$, IO_3^-, etc.) by hydrogen; and 3) the hydrogenation of organic compounds.

Of the salts studied, those of copper[2,44–54], silver[55–64], and mercury[65–67], and compounds of manganese (MnO_4^-),[68] molybdenum (MoO_4^{2-}),[69] and metals of the platinum group[70–73] were found to be active in aqueous solutions. Salts of copper[26,42,74–78] and silver[76,79] were also found to be active in solutions of amines. Salts of copper[80,81], silver, and mercury[82] are active in solutions of heptanoic acid and in biphenyl.

We shall not discuss these systems in the present review, since they have been examined in detail elsewhere[3,69,83,84]. It should be emphasised, however, that transition metal salts capable of catalysing the exchange and conversion of hydrogen and also the reduction of inorganic ions, may nevertheless not act as catalysts for the hydrogenation of organic compounds. Examples of such systems are provided by aqueous solutions of Cu^{II}, Ag^{I}, and Hg^{II} salts; in Halpern's opinion[85], there are two possible reasons for this: 1) these ions activate hydrogen but do not activate alkenes; 2) the ions themselves are reduced by hydrogen.

In some instances, however, reduction of transition metal salts by hydrogen does not take place in the presence of alkenes, and homogeneous hydrogenation of the alkenes takes place. Thus Flynn and Hulburt[86] observed the homogeneous hydrogenation of ethylene in the presence of the complex $C_2H_4.PtCl_2$. Precipitation of metallic platinum was observed as the ethylene was used up. In the present instance, complex formation with the alkene stabilises the valency state of the metal. An analogous picture is apparently observed in the homogeneous hydrogenation of maleic acid in the presence of $RuCl_3$ in an acidic aqueous solution[85] and in the hydrogenation of ethyl crotonate by means of palladium salts[87].

A curious feature is that in the catalytic reduction of oxidising ions $Cr_2O_7^{2-}$, IO_3^-, etc. by hydrogen in the presence of transition metal salts, the precipitation of metal is observed only after the oxidant is completely used up.

On the other hand, various transition metal ions which are not capable of activating hydrogen in ortho-para conversion or isotopic exchange may catalyse the hydrogenation of organic compounds. For example, aqueous solutions of Ni^{II} do not activate hydrogen[3], but hydrogenation of pent-2-ene and benzene takes place in aqueous $NiSO_4$ solution[88]. The apparent explanation is that the substrate first forms a complex with the metal salt, and this complex subsequently reacts with hydrogen. A large number of hydrogenating systems of this type involving transition metal salts was studied by Tulupov, who showed that solutions of the stearates and adipates of Ni^{II}, Fe^{III}, Co^{II}, Mn^{II}, Cr^{III}, and Zn^{II} in ethanol, liquid paraffin, and n-heptane catalyse the hydrogenation of cyclohexene and benzene (to cyclohexane), cyclohexanone (to cyclohexanol), and pentenes (to pentanes).[69,88-94] The rate of hydrogenation in the presence of transition metal salts under ordinary conditions is extremely low.

In the presence of copper and cadmium oleates under severe conditions (H_2 pressure 250–275 atm, temperature 260°C), unsaturated aliphatic acids are hydrogenated to the corresponding unsaturated aliphatic alcohols[95]. The hydrogenation of benzoquinone by means of copper acetate in quinoline[26] and of copper heptanoate in heptanoic acid solution[80] has been described. Rylander and coworkers[96] hydrogenated dicyclopentadiene, quinone-1,2, and naphthoquinone-1,4 by means of salts of metals of the platinum group in dimethylformamide (or dimethylacetamide) solution.

Finally, rhodium chloride in alcoholic solutions catalyses the homogeneous hydrogenation of hex-1-ene[97] and the hydrogenation of maleic acid to succinic acid[98] in acetamide.

b. Two-component Systems

Systems formed by the reaction of transition metal salts with reducing agents or with complex-forming reagents are much more effective catalysts for homogeneous hydrogenation than the transition metal salts themselves. This section deals with the $CoCl_2$–KCN system and catalysts of the Ziegler–Natta type. The investigation of the reaction mechanism and the nature of the active intermediate compound in these systems is an extremely complicated problem.

$CoCl_2$–KCN System. The absorption of hydrogen when potassium cyanide is added to an aqueous cobalt(II) chloride solution was first observed by Iguchi[99] in 1942, but this system only attracted special attention after the work of King[100] and Kwaitek[101,102].

Table 1. Hydrogenation of various substrates by means of the $CoCl_2$–KCN system in aqueous solutions (25°C; H_2 pressure = 1 atm).

Substrate	Reaction product	References
$[Fe(CN)_6]^{3-}$	$[Fe(CN)_6]^{4-}$	102
H_2O_2	H_2O	102
Ethylene	not hydrogenated	102
Propene	ditto	102
Cyclohexene	ditto	102,104
Styrene and substituted styrenes	ethylbenzene etc.	101,102,104
Propenylbenzene $CH_3CH{=}CHPh$	not hydrogenated	101
1,1-Diphenylethylene	not hydrogenated	101
Cyclohexene oxide	cyclohexanol	101
Styrene oxide	phenylethanol	101
Allyl chloride	propene	119
Butadiene	mixture of butenes	101,102,119–124,138
Isopropene	2-methylbut-2-ene	
	2-methylbut-4-ene	101,102,125,126
Cyclopentadiene	cyclopentene	102
1,3-Cyclohexadiene	cyclohexene	101,102
Unsaturated aldehydes (acrolein, tiglaldehyde, cinnamaldehyde)		101,102
Acrylic acid and its derivatives		101,102
Sorbic acid	2-hexenoic and 3-hexenoic acids	101,104,126–128
Cinnamic acid	phenylpropionic acid	101,104,118,129
Keto-acid oximes[a]		104,130–134
Keto-acids and keto-esters[a] (reductive amination)		104
Acetaldehyde[b]		102
Benzaldehyde	benzyl alcohol	102
$t\text{-}C_4H_9NO_2$	t-butylamine	136
Nitrobenzene and its derivatives	azoxy-, azo-, and hydrazobenzenes, aniline	102,135,139
Nitrophenols	aminophenols	136
Benzonitrile[c] etc.		136
Acrylonitrile[c]		136
Benzoquinone	hydroquinone	102
Azoxybenzene	azobenzene	101
Benzil	benzoin	101,104
Methylene Blue etc.		137

[a]Temperature 30–100°, H_2 pressure 50–100 at. [b]Condensation accompanied by absorption of hydrogen. Temperature of reaction 100°. [c]Reduction products not isolated, because they are hydrolysed.

The $CoCl_2$–KCN system can be used for the ready reduction of inorganic oxidising agents [H_2O_2, $Fe(CN)_6^{3-}$], benzoquinone, conjugated alkenes, unsaturated acids etc., and aliphatic and aromatic aldehydes (the reduction of aliphatic aldehydes is accompanied by condensation). Reductive amination of keto-esters also takes place in the presence of $CoCl_2$–KCN (see Table 1).

Monoalkenes[102-104] and non-conjugated dienes[102] are not hydrogenated under these conditions, however. α,β-Unsaturated acids and aldehydes show different behaviour on hydrogenation in the presence of the $CoCl_2$–KCN system[102]. Thus it was found that α-substituted acrylic acids—methacrylic, itaconic, and atropic acids—are hydrogenated quantitatively, but the corresponding aldehydes are not hydrogenated. On the other hand, crotonaldehyde is partly hydrogenated, and tiglaldehyde is quantitatively hydrogenated, whereas tiglic acid [*trans*-2-methyl-2-butenoic acid] is not hydrogenated at all. In the hydrogenation of acrylic acid at elevated temperature, it was unexpectedly found that α-methylglutaric acid is formed in addition to propionic acid.

The study of the extremely complicated process of complex formation in the $CoCl_2$–KCN system was begun by the work of Hume and Kolthoff[105] and Adamson[106]. Research workers have paid most attention to the problem of the nature of the complex activating the hydrogen (see for example Refs. 107–111). It has now been shown that the active species in the $CoCl_2$–KCN system is the complex $[Co^{II}(CN)_5]^{3-}$. The partial replacement of CN^- ligands in the complex $[Co(CN)_5]^{3-}$ by ethylenediamine produces new hydrogenation catalysts[112].

Griffith and Wilkinson[113,114] used the NMR method to detect the formation of a Co–H bond during the reduction of a solution of cobalt(II) chloride and KCN by sodium hydridoborate. A curious feature is that the hydrido-complex is present in the solution in concentrations of 3% even without treatment with $NaBH_4$.

King and Winfield[108] studied the ultraviolet spectra of cyanide solutions of cobalt salts after their reduction by hydrogen, $NaBH_4$, or electrolysis, and showed that in all instances a hydrido-complex with probable structure $[CoH(CN)_5]^{3-}$ ($\lambda = 305$ mμ) is formed. The formation of a hydridopentacyano-complex of cobalt was confirmed by De Vries[115], Burnett and coworkers[116], and others. This hydrido-complex was recently isolated in the form of the salt $NaCs_2CoH(CN)_5$.[117]

A number of authors[19,28,29,100,108] hold the view that the formation of the hydrido-complex $[CoH(CN)_5]^{3-}$ involves the simultaneous reaction of a hydrogen molecule with two molecules of the complex $[Co(CN)_5]^{3-}$ according to the scheme:

$$[Co] + [Co] \rightleftarrows [Co]_2; \quad [Co]_2 + H_2 \rightleftarrows 2H[Co]$$

where $[Co] = [Co(CN)_5]^{3-}$.

Simandi and Nagy[118] recently showed, however, that the activation of hydrogen is a two-stage process: a complex of H_2 with one molecule of the cyano-compound $[Co(CN)_5]^{3-}$ is formed first, after which rupture of the H–H bond in the complex takes place with the participation of a second $[Co(CN)_5]^{3-}$ anion:

$$[Co] + H_2 \rightleftarrows H_2 \cdot [Co]$$
$$H_2 \cdot [Co] + [Co] \rightleftarrows 2H[Co] \ .$$

CoF_2–NaF System. It has been reported[140] that the CoF_2–NaF system in water catalyses the hydrogenation of ethylene and butadiene.

Ziegler–Natta Catalysts. The reaction of compounds of transition metals (acetylacetonates etc.) with organometallic reducing agents (Alk_3Al, Et_3B, RMgBr, etc.) leads to the formation of soluble systems capable of catalysing the hydrogenation of various alkenes[141-148] at 30–50°C and a hydrogen pressure of 3–5 atm. The rate of hydrogenation by means of these systems is greater by several orders of magnitude than that for salts of transition metals without a reducing agent.

The metals can be arranged in the following order of decreasing activity in these systems[141,147]: Ni ≥ Co > Cu ≥ Fe > Mn ≥ Cr > V, and that the activity of the catalyst decreases with increase in the acceptor power of the ligands[147]. The rates of hydrogenation of mono- and disubstituted alkenes are approximately the same, but much greater than the rates of hydrogenation of trisubstituted and more particularly tetrasubstituted alkenes. Compounds containing a carbonyl group (ketones and aldehydes), and also compounds containing nitrile, nitro, azo, and other functional groups are not hydrogenated in the presence of these catalysts.

The hydrogenation of alkenes by means of these catalysts involves the initial formation of a compound with a transition metal–carbon bond, and hydrogenolysis of this compound gives the final product and the transition metal hydride[141,142,147] according to the scheme:

$$R_3Al + MX_n \rightarrow R_3AlX + RMX_{n-1}$$
$$RMX_{n-1} + H_2 \rightarrow RH + HMX_{n-1}$$
$$\begin{array}{c} | \quad | \\ C{=}C \\ | \quad | \end{array} + HMX_{n-1} \rightarrow \begin{array}{c} | \quad | \\ HC{-}C{-}MX_{n-1} \\ | \quad | \end{array}$$
$$\begin{array}{c} | \quad | \\ HC{-}C{-}MX_{n-1} \\ | \quad | \end{array} + H_2 \rightarrow \begin{array}{c} | \quad | \\ HC{-}CH \\ | \quad | \end{array} + HMX_{n-1}$$

or

$$\begin{array}{c} | \\ HC{-}CHX_{n-1} \\ | \end{array} + HMX_{n-1} \rightarrow \begin{array}{c} | \quad | \\ HC{-}CH \\ | \quad | \end{array} + (MX_{n-1})_2$$
$$(MX_{n-1})_2 + H_2 \rightarrow 2\,HMX_{n-1} \ .$$

Systems of this type can also be used for the hydrogenation of aromatic compounds. Thus Lapport and Schuett[149] showed that a solution of Et_3Al and Ni^{II} 2-ethylhexanoate in heptane or in benzene is an excellent catalyst for the hydrogenation of various aromatic compounds (150°C, 70–80 atm H_2).

The hydrogenation of aromatic derivatives by means of catalysts of the Ziegler–Natta type is apparently accompanied by the intermediate formation of a π-complex. In the opinion of Kalechits and coworkers[150], evidence of this is provided by the fact that hydrogenation takes place under conditions in which π-complexes are formed.

Catalysts of the Ziegler–Natta type also hydrogenate compounds with conjugated double bonds[151] and oils[152].

Individual Transition Metal Complexes

A large number of individual transition metal complexes capable of catalysing homogeneous hydrogenation are now known; the activities of some of these are greater than that of the most active of the catalysts examined in previous sections. The use of these catalysts has played an exceptionally important part in the investigation of the mechanism of hydrogenation, since the compositions and structures of these complexes have in most instances been reliably established.

Metal Carbonyls and Their Derivatives. Hydrogenation by means of metal carbonyls is closely related to hydroformylation. Hydrogenation generally takes place under the same conditions as hydroformylation (a high pressure of "synthetic" gas—a mixture of CO and H_2—ensures the presence of carbonyls in the reaction mixture). The hydrogenating power of various carbonyl hydrides has been briefly discussed by Davydov[153].

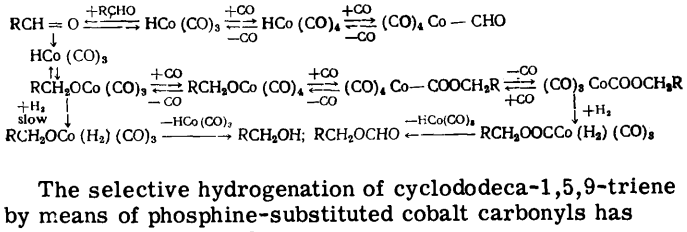
The hydrogenating power of cobalt carbonyl has been most extensively studied[154]. The ratio of the rates of the parallel reactions of hydroformylation and hydrogenation depends on the structure of the substrate. Thus simple alkenes give saturated aldehydes and the corresponding alcohols[155-159]; α,β-unsaturated ketones and aldehydes are hydrogenated to saturated carbonyl derivatives[155,160,161]; and conjugated alkenes give both hydrogenation products and hydroformylation products[154].

Cobalt carbonyl has been used for the hydrogenation of aldehydes[154,155,157,158,162-164], ketones[155,165], alcohols[155,160,165-169], aromatic compounds[155,166,170], azobenzene[171], poly-unsaturated acids[172], etc.

Two possible routes for the activation of hydrogen during hydrogenation by means of cobalt carbonyl have been discussed[154,160,162]: a) $Co_2(CO)_8 + H_2 \rightleftharpoons CoH(CO)_4$, that is the formation of cobalt hydride as homogeneous catalyst, and b) heterogeneous hydrogenation on metallic cobalt, formed by decomposition of the carbonyl:

$$Co_2(CO)_8 \rightleftarrows 2Co^0 + 8\,CO.$$

It may be taken that the homogeneous nature of catalytic hydrogenation by means of $Co_2(CO)_8$, in which the hydrogenating agent is $CoH(CO)_4$, has now been proved. This scheme involving the participation of $CoH(CO)_4$ was adopted, for example, by Marko[164] to explain the formation of alcohols in the hydrogenation of aldehydes. The same scheme explains the presence of a certain amount of formates in the reaction mixture.



The selective hydrogenation of cyclododeca-1,5,9-triene by means of phosphine-substituted cobalt carbonyls has also been described[173].

Recent work has shown that not only cobalt carbonyls, but also the carbonyls of other metals, can act as catalysts for homogeneous hydrogenation. Thus Imyanitov and Rudkovskii[174] studied the hydrogenation of alkenes in the presence of rhodium and iridium carbonyls. Hydroformylation takes place in parallel.

Heil and Marko[175], under the conditions of formation of rhodium carbonyl from $RhCl_3$, hydrogenated aliphatic aldehydes and benzaldehyde to the corresponding alcohols. Hept-1-ene and cyclohexene under these conditions first undergo hydroformylation, and are then hydrogenated to octanol and cyclohexylcarbinol.

The iron carbonyl $Fe(CO)_5$ is an effective catalyst for the homogeneous hydrogenation of poly-unsaturated fats. The hydrogenation of soya-bean oil in the presence of iron carbonyl at 180°C and 7–70 atm H_2 has been reported by Frankel and coworkers[176-178].

A complex of iron carbonyl with linoleate was isolated in the hydrogenation of methyl linoleate[177], and this complex was found to be a better hydrogenation catalyst than the original $Fe(CO)_5$.

The selective hydrogenation of unsaturated esters by means of π-complexes of $Fe(CO)_5$ [179-181] and by means of π-complexes of chromium carbonyl[182] has been described. In both instances the authors cited suggest that during the reaction these π-complexes dissociate with the formation of the species $Fe(CO)_3$ and $Cr(CO)_3$ respectively. The reaction of these species with hydrogen gives the hydrides $FeH_2(CO)_3$ and $CrH_2(CO)_3$, which then react with the substrate. Frankel[182] showed that the two hydrogen atoms are transferred to the substrate simultaneously.

Japanese workers[183] studied the mixed cyclopentadienylcarbonyl complex $Cp_2Ti(CO)_2$ as hydrogenation catalyst. They used this catalyst to hydrogenate various acetylenic derivatives in a hydrocarbon medium under comparatively mild conditions (50–65°C and H_2 pressure 50 atm). It was found that the rates of hydrogenation depend on the nature of the substituents R, decreasing in the order Ph > t-butyl > n-alkyl for the monosubstituted acetylenes RC≡CH or in the order Ph > n-alkyl for the disubstituted RC≡CR. Conjugated dialkenes have been hydrogenated by means of the π-complexes of iron, nickel, and cobalt carbonyls[151].

Complexes of Group VIII Metals with P-containing Ligands. In 1962, Vaska and coworkers[184] found that iridium complexes of the type $IrCl(CO)(Ph_3P)_2$ absorb molecular hydrogen reversibly at room temperature and atmospheric pressure with the formation of hydrides stable in air. Later, they also showed that hydrido-complexes of the type $IrH(CO)(Ph_3P)_3$ are effective catalysts for the homogeneous hydrogenation of ethylene[185,186]. The hydrogenation of alkenes is also catalysed by complexes of the type $IrHX_2L_3$, where X = Hal, L = PPh_3, Ph_3As, or Ph_3Sb;[187] alkenes with a terminal double bond are hydrogenated more rapidly than disubstituted alkenes, and further branching of the alkene chain leads to an even more marked decrease in the rate of hydrogenation. The use of iridium complexes as hydrogenation catalysts is also described in the patent literature[188,189]. In the presence of $IrH_3(PPh_3)_3$, aldehydes are hydrogenated with the formation of alcohols[190]. Unlike the iridium complex $IrCl(CO)(Ph_3P)_3$, the rhodium complex $RhCl(CO)(Ph_3P)_3$ was found to be inactive under the same conditions[185]. In a study of the hydroformylation of alkenes by means of $RhCl_3(Ph_3P)_3$, Osborn and coworkers[191,192] found that at high temperatures and pressures of the CO + H_2 mixture (1 : 1) the aldehyde obtained is converted into the alcohol. The complex $RhCl(Ph_3P)_3$ is an even more effective hydrogenation catalyst[193]. This catalyst has been used to hydrogenate a number of alkenes and alkynes (see Table 2); the rate of hydrogenation of the triple bond was found to be less than that of the double bond. As in the hydrogenation of alkenes, steric hindrance has a significant influence on the rates of hydrogenation of alkynes and the duration of the induction period.

Organic compounds with functional groups—ketones (aldehydes), alcohols, carboxylic acids, nitriles, chlorides, and nitro-compounds—are not hydrogenated in the presence of $RhCl(Ph_3P)_3$.[193] Butadiene and cyclo-octa-1,3-diene are hydrogenated only at 60°C, but are not hydrogenated at room temperature.

Non-conjugated dienes with double bonds in terminal positions (octa-1,7-diene) are hydrogenated more rapidly than hex-1-ene, which in turn is hydrogenated more rapidly than hex-2-ene; cis-alkenes are hydrogenated more rapidly than the trans-isomers. Unlike propene, ethylene is not hydrogenated under these conditions. The rate of hydrogenation depends on the concentration of substrate and catalyst, the H_2 pressure, and temperature, and increases considerably when a polar solvent is used. The addition of such complex-forming reagents as triphenylphosphine, thiophen, 8-quinolinol, pyridine, and acetonitrile decreases the reaction rate; ethylene, conjugated dienes, and O_2 poison the catalyst.

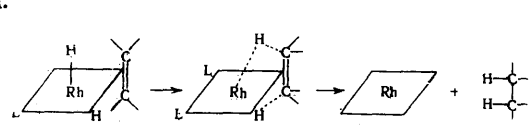
It has been shown that in the hydrogenation of alkenes in the presence of $RhCl(Ph_3P)_3$ the active compound is the dihydride $Rh(H_2)Cl(Ph_3P)_2$; one molecule of catalyst takes part in the transfer of hydrogen to the alkene.

Table 2. Hydrogenation of organic compounds in the presence of phosphine complexes of transition metals (25°C, H_2 pressure 1 atm).

Complex	Compound hydrogenated	Reaction product	References
$RhX(Ph_3P)_3$, where X = Cl, Br, or I	Ethylene	not hydrogenated	193, 194
	Alkenes (propene, butenes, hexenes, stilbene, etc.)	alkanes	193, 194, 202, 203, 206, 207
	Dienes	alkanes	193
	Maleic and fumaric acid	succinic acid	193
	Alkynes	alkenes + alkanes	193, 203
	Acetylenedicarboxylic acid		193
	Aliphatic-aromatic and higher aliphatic unsaturated acids; higher aldehydes, etc.	not hydrogenated	202, 203
	Steroids		203, 204
	Quinones		205
$RhCl_3(Ph_3P)_3$[a]	Heptaldehyde	heptyl alcohol	191
$RhH(CO)(PPh_3)_3$	Ethylene	ethane	185, 208
	Hex-1-ene	hexane	
$IrH(CO)(PPh_3)_3$	Ethylene	ethane	185
	Acetylene	ethylene + ethane	
$Ir(H)Cl_2(Ph_3P)_3$ $Ir(H_2)Cl(Ph_3P)_3$	Norbornadiene	not hydrogenated	148
$RhX(CO)(Ph_3P)_2$	Ethylene	ethane	209
$IrX(CO)(Ph_3P)_2$	Propene	propane	209
	Acetylene[b]	ethylene + ethane	
	Alkenes	alkanes	
	Alkynes	alkenes + alkanes	
$[Ir(Ph_2PCH_2CH_2PPh_2)_2]Cl$	Butyraldehyde	butanol	210
$[Rh(Ph_2PCH_2CH_2PPh_2)_2]Cl$	Acetylenes	olefins + paraffins	210
$H_3Ir(PPh_3)_3$[b]	Butyl aldehyde	Butyl alcohol	190
$RuCl_2(Ph_3P)_4$ $RuCl_2(Ph_3P)_3$	Hept-1-ene	heptane	195
$RuHCl(Ph_3P)_3$	Cyclopentene	cyclopentane	196, 211
	Cyclohexene	cyclohexane	
	Cyclo-octene	cyclo-octane	
	Tolane	cis-stilbene	
$OsHCl(CO)(Ph_3P)_3$	Acetylene[c]	ethylene + ethane	185

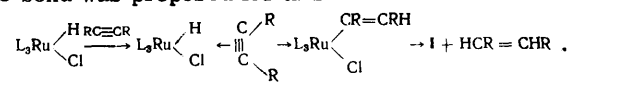
[a]Temperature 100°, H_2 pressure 50 atm. [b]Temperature 60°. [c]Temperature 50°; solvent—acetic acid.

The following hydrogenation scheme with simultaneous transfer of two hydrogen atoms to the substrate was proposed:



Complexes of rhodium with Ph_3As and more particularly Ph_3Sb ligands were found to be much less effective catalysts[194].

Evans and coworkers[195] showed that hept-1-ene and hex-1-yne are readily hydrogenated in the presence of ruthenium complexes of the type $RuCl_2L_4$ and $RuCl_2L_3$, where L = Ph_3P (at 25°C and 1 atm). A mechanism involving the formation and subsequent hydrogenolysis of an Ru–C bond was proposed for this reaction[196].



(I)

Alkyl phosphite complexes of univalent cobalt $CoXL_3$ and $CoXL_4$, where L = $(EtO)_3P$ and X = Cl, Br, or I, absorb hydrogen under mild conditions and act as catalysts for the hydrogenation of alkynes and various alkenes with activated double bonds (vinyl ethyl ether, vinyl acetate, etc.).[198,199]

The following scheme was proposed for the hydrogenation of alkynes by phosphite complexes of cobalt (in alcohol):

$$L_4CoCl + H_2 \rightarrow L_4CoH + HCl \quad (1)$$

$$L_4CoH + RC \equiv CH \rightarrow L_4CoH \quad (2)$$

$$L_4Co - H \rightarrow L_4Co - CH = CHR \quad (3)$$

$$L_4Co - CH = CHR \xrightarrow{H_2} L_4CoH + H_2C = CHR \quad (4a)$$

$$L_4Co - CH = CHR \xrightarrow{R'OH} L_4CoOR' + H_2C = CHR \quad (4b)$$

$$L_4CoOR' + H_2 \rightarrow L_4CoH + R'OH \quad (5)$$

To determine whether hydrogenation takes place with hydrogenolysis (4a) or alcoholysis (4b) of the intermediate compound with the Co–C bond, C_2H_5OD was used as solvent. It was found that the hydrogenation product did not contain deuterium. Thus the molecular hydrogen is the source of both hydrogen atoms in the hydrogenation of alkynes (scheme 4a). An interesting feature is that an alkyl phosphite complex of zero-valent cobalt[200] did not catalyse hydrogenation even at 150°C and a hydrogen pressure of 120 atm.

It was recently found[201] that the complex $CoH_2(Ph_3P)_3$ catalyses the hydrogenation of ethylene.

Complexes Containing the $SnCl_3$ Ligand. Cramer and coworkers[212] were the first to carry out the homogeneous hydrogenation of ethylene in an alcoholic solution of K_2PtCl_4 and $SnCl_2$ (H_2 pressure 1 atm, 25°C). This system also catalyses the hydrogenation of pent-1-ene[213], cyclohexene[214], and other alkenes[215]. In the hydrogenation of acetylene[212], a mixture of ethylene and ethane is formed. Cramer and coworkers[212] were able to isolate a compound containing a Pt–$SnCl_3$ bond and to show that $SnCl_2$ plays a dual role in complex formation in this system: 1) it promotes the coordination of ethylene to platinum; and 2) it stabilises the valency state of platinum relative to reduction by hydrogen.

Bailar and coworkers[216–219] showed that complexes of the type MX_2L_2 (where L = R_3P, R_3As, etc., X = Hal, and M = Ni, Pd, or Pt) in the presence of $SnCl_2$ are capable of catalysing the selective hydrogenation of compounds with two or more double bonds to compounds with a single isolated bond.

Khrushch and coworkers[220,221] studied the reaction kinetics and isotopic composition of the products of the hydrogenation of ethylene by means of platinum complexes of this type in the $C_2H_4 + D_2 + CH_3OH$ and $C_2H_4 + H_2 + CH_3OD$ systems, and found that in both instances the chief product is C_2H_5D. This shows that in the hydrogenation,

one of the hydrogen atoms is provided by the H_2 molecule and the other by the alcohol, according to the scheme:

$$[Pt] + C_2H_4 \rightleftarrows Pt(C_2H_4)$$

$$Pt(C_2H_4) \overset{H_2}{\rightleftarrows} \left[\begin{matrix} H \\ H \end{matrix}\!\!>\!PtC_2H_4\right] \rightleftarrows [^-HPtC_2H_4] + H^+$$

$$[^-HPtC_2H_4] \rightleftarrows PtC_2H_5^-$$

$$PtC_2H_5^- + H^+ \rightarrow [Pt] + C_2H_6$$

where [Pt] represents the active complex.

The complex $PtHCl(Ph_3P)_2$ in the presence of $SnCl_2$ catalyses the hydrogenation of norbornadiene and hex-3-yne-2,5-diol. The complex $Ir(H_2)(SnCl_3)(Ph_3P)_3$ does not exhibit hydrogenating power[196].

Complexes with Other Ligands. The influence of nitrogen-containing ligands (ammonia and amines) on the activity of hydrogenation catalysts has been studied.

Iguchi[222] observed the precipitation of metal in the hydrogenation of quinone, cinnamic acid, and other compounds in the presence of complexes of rhodium with ammonia.

A number of authors[8,62] have studied the influence of amines as ligands on the reduction of Ag^+ by hydrogen. It was found that the reactivity of the corresponding ionic complex decreases in the following order of ligands:

$$R_3N > R_2NH > RNH_2 > NH_3$$

The reaction of hydrogen with the complex $RhCl_3Py_3$ gives a hydride with assumed composition $RhHCl_2Py_3$, which hydrogenates hex-1-ene[223].

A number of effective catalysts for homogeneous hydrogenation have been prepared by Khidekel' and coworkers. Thus solutions of complexes of transition metals (Rh, Ru, Ir, or Mo), stabilised by π-donor quinonoid and aromatic ligands (duroquinone, mesitylene, etc.) in dimethylformamide (25°C, H_2 pressure 1 atm) catalyse the hydrogenation of alkenes; the activity of these catalysts is greater by several orders of magnitude than that of heterogeneous catalysts (rhodium on carbon, etc.).[224,225]

The reduction of rhodium salts in the presence of aminoacids (L-tyrosine, α-phenylalanine, etc.) and peptides leads to the formation of Rh^I complexes, which are extremely effective catalysts for the hydrogenation of unsaturated compounds under mild conditions[226-228]. An important property of the complexes of rhodium with aminoacids is their ability to catalyse the hydrogenation of aromatic compounds under mild conditions (anthracene > benzene > naphthalene).[229] When the ligand has an asymmetric centre (the complex with L-tyrosine), acetoacetic ester undergoes asymmetric hydrogenation to ethyl β-hydroxybutyrate[229]. According to the data obtained, these catalysts show a marked similarity to the enzyme hydrogenase.

The study of the structures of these complexes has shown that they are of the half-sandwich type, the aromatic ring of the aminoacid acting as π-ligand.

IV. GENERAL SYSTEMATIC FEATURES AND MECHANISM OF THE ACTIVATION OF HYDROGEN AND HOMOGENEOUS HYDROGENATION

Comparison of the results of the study of a number of catalytic systems makes it possible to distinguish various common regular features of homogeneous hydrogenation and the activation of hydrogen in the presence of transition metal complexes and to examine the part played by the transition metal and the ligands, the influence of solvents, the stereospecificity and selectivity of the catalysts, etc.

1. ACTIVATION OF MOLECULAR HYDROGEN BY TRANSITION METAL COMPLEXES

a. The Part Played by the Transition Metal

The H_2 molecule is a fairly inert molecule with a closed electron cloud, and its dissociation energy is 104 kcal mole^{-1}.

The activation of H_2 by transition metal compounds involves the reaction of the hydrogen molecule with the ion (or complex) of the metal; the H–H bond in the transition state (or in the intermediate compound) is weakened and then broken.

There are thus two possibilities in the activation of hydrogen. According to the first, the H_2 acts as electron donor, that is the bonding electrons of the hydrogen are partly transferred to vacant orbitals of the metal ion (donor–acceptor bond).[230] The other possibility in the activation of H_2 is that an electron is transferred from the metal atom rich in electrons to an antibonding orbital of the hydrogen molecule (dative bond), that is H_2 acts as an electron acceptor (in Halpern's opinion[230], this process may involve the $2p$ orbitals of the hydrogen). Dative bond formation makes it possible to explain the activation of hydrogen not only by ions (or complexes) of metals rich in electrons[193], but also by such ions as OH^-, NH_2^-, R^-, etc.[231]

Thus the transition states (or intermediate compounds) of these two extreme types, depending on whether hydrogen acts as electron donor or electron acceptor, can be represented as $M.....H_2^+$ and $M.....H_2^-$. The energies of rupture of the H–H bonds in the corresponding molecular ions H_2^+ and H_2^- are not the same and have the values 62 kcal mole^{-1} and 3.4 kcal mole^{-1} (or 18.6 kcal mole^{-1} according to other data) respectively[232].

Syrkin[233] suggested that in the activation of H_2 with the formation of a bond of the donor–acceptor type, a three-centre transition state with two electrons in the field of three nuclei may be realised:

$$M^+ : \begin{matrix} \cdot H \\ \vdots \\ \cdot H \end{matrix}$$

For a transition state of the type $M.....H_2^+$ to be realised in the activation of hydrogen, the M atom must have suitable vacant orbitals with sufficiently low energy. For transition metals these are primarily d orbitals.

In the earliest reviews of the homogeneous activation of hydrogen it was noted that the active species are primarily transition metal ions with a filled or almost filled d electron level[3]:

$$Cu^{II} - 3d^9;\ Cu^I - 3d^{10};\ Pd^{II} - 4d^8;\ Ag^I - 4d^{10};\ Hg^{II} - 5d^{10}$$

It is significant that for ions with a filled d level the difference in the energies of the d orbitals and the next vacant s and p orbitals is comparatively small, and the ease of the $d \rightarrow s$ and $d \rightarrow p$ transitions leads to the production of vacant d orbitals. It is interesting in this connection to note that although the ions Zn^{2+}, Cd^{2+}, and Hg^{2+} have similar d^{10} electronic configurations, only the Hg^{2+} ion is effective in the activation of hydrogen, since the difference in the energies of the d orbitals and the higher s orbital is much smaller for this ion than for the other ions of this series[8].

On the other hand, the formation of a dative M.....H_2^- bond, that is transfer of the electrons of the M atom to an antibonding molecular orbital of hydrogen, is favoured by a minimal positive charge on the metal. This explains the higher activating power of Cu^I compared with Cu^{II} in the reaction with hydrogen. A large proportion of catalysts for homogeneous hydrogenation known at present are compounds of transition metals with a low oxidation state.

Another factor facilitating the formation of dative bonds is the presence of electron-donating ligands on the metal atom. Thus the activation of hydrogen may be favoured by the presence of vacant orbitals and by a low degree of oxidation of the metal in the complex.

b. The Part Played by the Ligands and Solvent

A significant influence on the catalytic activity of a complex is shown by the nature of the ligands attached to the metal atom. The ability of various ligands to form both donor–acceptor bonds and dative bonds leads to the stabilisation of low valency states of the metal. Thus for example ligands of the type PR_3 can use the unshared pair of electrons of the tervalent phosphorus to form a donor–acceptor bond, and can use vacant *d* orbitals with comparatively low energy to accept electrons from the metal atom. Ligands of this type stabilise rhodium complexes[193] which absorb hydrogen reversibly and catalyse the homogeneous hydrogenation of organic compounds. With the analogous complexes formed by rhodium with amines, which are not capable of forming dative bonds, hydrogenation is accompanied by the formation of a metallic precipitate. The preferential formation of bonds of a given type by different ligands makes it possible to increase or decrease the electron density at the metal atom in the reaction with hydrogen or the substrate and thus to ensure the optimal conditions for the manifestation of catalytic properties by the complex. An interesting feature here is that the catalytic activity of rhodium complexes which absorb hydrogen readily and reversibly is extremely sensitive to small changes in the donor–acceptor properties of the ligand: the replacement of a phenyl group in triphenylphosphine by an ethyl group reduces considerably the activity of the rhodium complex[206] in hydrogenation.

A decrease in the positive charge of a metal ion is also brought about by its reaction with an anion acting as ligand. It is important, however, that the bond between this ligand and the metal ion be sufficiently labile to ensure the ready liberation of a coordination position for the H_2 molecule in the reaction with hydrogen. Thus for example silver acetate and sulphate are catalytically active, whereas the trifluoroacetate, chloride, and other silver salts are inactive. The catalytic activity of copper acetate and chloride, and also of $HgSO_4$, is greater than that of the corresponding salts with less nucleophilic anions.

A coordination position may also be vacated by dissociation of a complex, as shown by the complexes $RhCl(Ph_3P)_3$,[193] $RuCl_2(Ph_3P)_4$,[195] etc. This vacant position is apparently occupied by a solvent molecule, which is readily displaced by hydrogen. An attempt by Halpern[3] to correlate the catalytic activities of various metals with their stability constants is of interest in this connection.

The importance of a vacant (or readily liberated) coordination position for the catalytic activity of a complex in homogeneous hydrogenation can be demonstrated by a number of other examples. Thus the Cu^{2+} ion is active in aqueous medium, but its catalytic activity is decreased by the addition of chelating reagents which "screen" the orbitals accessible to hydrogen, and the catalytic activity may disappear completely at high concentrations of the chelating agent[52].

The catalytic activity of the complexes of rhodium and iridium with bidentate ligands $[Rh(Ph_2PCH_2CH_2PPh_2)_2]Cl$ and $[Ir(Ph_2PCH_2CH_2PPh_2)_2]Cl$ is much smaller than that of the corresponding complexes with unidentate ligands $RhCl(Ph_3P)_3$ and $IrCl(CO)(Ph_3P)_2$.[220] In the opinion of the authors cited, the chelate complexes form a very stable adduct with hydrogen, and this prevents further hydrogenation.

Triphenylphosphine complexes of rhodium react with such compounds as CO, $CH_2=CH_2$, $CF_2=CF_2$, and tolane to form complex compounds which are so stable that they do not activate hydrogen[193]. This explains the "poisoning" of rhodium catalysts by ethylene and carbon monoxide.

Thus in homogeneous hydrogenation the part of ligands may be played not only by groups introduced beforehand, but also by molecules of the substrate, reaction products, hydrogen, and the solvent.

The functions of the solvent in catalytic systems may be extremely varied. Thus the solvent takes direct part in complex formation. With strong electrolytes, such as aqueous solutions of perchlorates, the metal ion is solvated by water. (The absence of a perchlorate salt effect when copper perchlorate is used as hydrogenation catalyst indicates that it is the Cu^{II} ion, and not a perchlorato-complex of copper, which is active in this reaction.) Measurements of the molecular weight of copper acetate in pyridine and dodecylamine led Wright and coworkers[76] to suggest that the copper salt exists in the form of a complex in solutions of effective complex-forming reagents such as amines. This complex formation with the solvent explains the marked influence of substituents in quinoline and pyridine on the catalytic activity of Cu^{II} in these solvents[27,77]. Thus the introduction of a methyl group into the pyridine molecule leads to a significant increase in the activity of copper acetate compared with the activity of this salt in pyridine.

It has been suggested[193] that the rhodium complex $RhCl_3(Ph_3P)_3$, which dissociates readily in benzene, subsequently reacts with hydrogen and a substrate in the form of a solvated four-coordinated complex $RhCl(Ph_3P)_2(Sol)$, where Sol represents a solvent molecule. In the opinion of the authors cited, this is confirmed by the fact that hydrogenation does not take place in solvents which are more powerful complex-forming reagents. An interesting feature is that a fairly stable complex with the composition $Rh(H_2)Cl(AsPh_3)_2.0.5CH_2Cl_2$ was isolated from solutions of the analogous complex of rhodium with Ph_3As in CH_2Cl_2.[194]

The nature of the solvent has a significant influence on the nature of the rupture of the H–H bond in the hydrogen molecule. Thus in the activation of hydrogen by solutions of copper and silver salts in amines, heterolytic splitting of the hydrogen predominates over homolytic splitting in the absence of aqueous solutions of these salts. In Halpern's opinion, this is partly due to the fact that a solvent more basic than water combines with the H^+ ions formed.

Heterolytic rupture of the H_2 is facilitated not only by greater basic strength of the solvent but also by dilution of the solution and increase in temperature[56].

There is no doubt that the stability and hence the activity of the hydride formed by the reaction of hydrogen with the transition metal complex also depends to a marked extent on the nature of the solvent. In many instances the hydrogen atom of the hydride takes part in exchange reactions with the solvent, and this may have a significant influence on the kinetics and yield of reaction products.

In some instances it has been shown that a solvent containing labile hydrogen can take direct part in one of the hydrogenation stages by acting as a source of one of the H atoms, as for example with platinum complexes [221]:

$$^{-}H[Pt] + C_2H_4 \rightarrow PtC_2H_5^-$$
$$PtC_2H_5^- + ROH \rightarrow C_2H_6 + [Pt] .$$

The part played by ethanol in the catalytic reactions of complexes of Group VIII metals is considerable, and many of its aspects are not clear. The rhodium complexes mentioned above are more active when ethanol is introduced into the non-polar solvent; the efficiency of the $CoCl_2$–KCN system is greatly increased in alcoholic solutions; phosphite complexes of cobalt are also active only in the presence of alcohols [197]; and ruthenium complexes do not catalyse hydrogenation in the absence of traces of alcohol [195]. It should also be noted that side reactions involving alcohols may also deactivate a catalytic system: at elevated temperatures, the complex $RhCl(Ph_3P)_3$ may decarbonylate alcohol and be converted into the inactive $RhCl(CO)(Ph_3P)_3$. [193]

c. Mode of Activation of Molecular Hydrogen

The various possible reactions involved in the activation of hydrogen can be represented schematically as follows:

1) Heterolysis: $RuCl_6^{3-} + H_2 \rightleftharpoons RuHCl_5 + H^+ + Cl^-$
2) Homolysis: $2Co(CN)_5^{3-} + H_2 \rightarrow 2CoH(CN)_5^{3-}$
3) Insertion: $IrCl(CO)L_2 + H_2 \rightarrow IrCl(H_2)(CO)L_2$
4) Electron transfer: $Hg^{2+} + H_2 \rightarrow Hg^0 + 2H^+$.

Insertion, which is of independent interest, may also apparently be an intermediate stage in the homolytic or heterolytic splitting of hydrogen, for example:

$$MXL_n + H_2 \rightarrow M(H_2)XL_n \rightarrow MHL_n + HX \text{ etc.}$$

Published data indicate that activation of hydrogen may take place on a single metallic centre or on two such centres. In the latter instance the metal atoms may be the same, as in $Co_2(CO)_8$, [154] or different, as in complexes with a Pt–Ge bond [234]; the lowest value for the activation of rupture of the H–H bond (9 kcal mole^{-1}) was observed when these complexes were used. In some instances, ligands such as amines may act as second centre for the activation of hydrogen, for example:

$$(L{-}Ag{-}L)^+ + H_2 \rightarrow \left[\begin{matrix} L{-}Ag^+{-}L \\ \vdots \quad\quad \vdots \\ H^{-\delta} \ldots H^{+\delta} \end{matrix}\right] \rightarrow AgHL + H^+$$

where L represents an amine.

2. TRANSITION METAL HYDRIDES TAKING PART IN CATALYTIC REACTIONS OF HOMOGENEOUS HYDROGENATION

The intermediate formation of a hydride in the reaction of hydrogen with an active complex is the most important stage in catalytic hydrogenation. The study of the properties of hydride complexes of transition metals and their behaviour under the conditions of hydrogenation is of considerable assistance in reaching an understanding of the reaction mechanism.

In the earliest work on the activation of hydrogen, the intermediate formation of hydrides was assumed merely on the basis of kinetic and thermodynamic data (with the exception of CuH, which was actually prepared), but the position has now altered significantly. It has been possible to isolate a number of hydrides in the form of individual compounds. To confirm the formation of hydrides in the reaction mixture and to obtain information on their structures, extensive use is made of infrared spectroscopy and proton magnetic resonance spectroscopy [235,236].

The stability of hydride complexes depends to a marked extent on the nature of the metal, the ligand, and the solvent; the nature of the H atom in these complexes varies from strongly acidic in $CoH(CO)_4$ to labile hydrido in $PtHCl(Ph_3P)_2$.

The hydrogen in the hydride complex should be sufficiently labile to take part in hydrogen transfer with subsequent regeneration of the complex, capable of activating hydrogen again.

Hydride complexes with one, two, or three hydrogen atoms on one metallic centre are now known. In the discussion of reaction mechanisms, allowance must be made for the fact that with di- and tri-hydrides the hydrogen atoms may not be transferred to the substrate molecule simultaneously, since the properties of these H atoms may be different. Osborn and coworkers [193] discuss the alternative possibilities of simultaneous or consecutive transfer of hydrogen for the rhodium dihydride $Rh(H_2)Cl(Ph_3P)_2$.

Some authors regard the reaction of hydrogen with a transition metal complex as formal oxidation of the metal by hydrogen [184]:

$$Ir^{I}Cl(CO)(Ph_3P)_2 + H_2 \rightleftharpoons Ir^{III}(H_2)Cl(CO)(Ph_3P)_2$$
$$2[Co^{II}(CN)_5]^{3-} + H_2 \rightleftharpoons 2[Co^{III}H(CN)_5]^{3-} \text{ (Ref.108)}$$

With increase in the valency of the metal there is an increase in its coordinating power, and both these factors have a direct influence on the stability of the resulting hydride [235]. Vaska [185] suggests that in homogeneous hydrogenation by means of the hydrido-complex $IrH(CO)(Ph_3P)_3$ this monohydrido-compound reacts with H_2 with the formation of the even more active seven-coordinated trihydrido-compound $IrH_3(CO)(Ph_3P)_3$, which subsequently reacts with the substrate.

In the reaction of H_2 with the osmium complex $OsHL_5$ (where L represents a ligand), the 8-coordinated OsH_3L_5 is formed [185]. Complexes of this kind with an unusual coordination number are unstable and should give up hydrogen readily. In Vaska's opinion, it is necessary in the prediction of the catalytic activity of complexes to consider the relative stabilities of their electronic and stereochemical configurations, and also the stabilities of their potential active adducts with hydrogen, such as OsH_3L_5, $IrH_3(CO)L_3$, [185] or the proposed unstable 5-coordinated complex $[PtHCl_2(SnCl_3)(C_2H_4)]^{2-}$. [221]

Most catalysts of homogeneous hydrogenation absorb hydrogen reversibly. This property of complexes (or salts) is not essential, however, for the manifestation of catalytic power. Thus the complex $RhH(CO)(Ph_3P)_3$ does not absorb H_2, but it catalyses the hydrogenation of ethylene [208]. This is apparently due to the fact that the complex (in the present instance a hydrido-complex) first reacts with the substrate, and then activates hydrogen (hydrogenolysis of the metal–carbon bond).

3. ACTIVATION OF THE SUBSTRATE AND TRANSFER OF HYDROGEN

In hydrogenation it is possible to distinguish stages involving the activation of hydrogen, the activation of the substrate, and the transfer of hydrogen to the substrate.

In general, the sequence of these stages can be represented by the following basic schemes[69] (M represents the transition metal complex, and S the substrate):

Scheme I:

$$M + H_2 \rightleftarrows M\cdot H_2 \quad (a)$$

$$M\cdot H_2 + S \rightleftarrows S\cdot M\cdot H_2 \quad (b)$$

$$S\cdot M\cdot H_2 \rightarrow S\cdot H_2 + M \quad (c)$$

According to scheme I, activation of hydrogen takes place first with formation of a hydride, which then reacts with the substrate and hydrogen is transferred to the substrate.

Scheme II:

$$M + S \rightleftarrows M\cdot S \quad (a)$$

$$M\cdot S + H_2 \rightleftarrows H_2\cdot M\cdot S \quad (b)$$

$$H_2\cdot M\cdot S \rightarrow S\cdot H_2 + M \quad (c)$$

According to scheme II, the complex with the substrate is formed first, and this complex then activates hydrogen.

Scheme III:

$$M + S \rightleftarrows M\cdot S \quad (a)$$

$$M' + H_2 \rightleftarrows M\cdot H_2 \quad (b)$$

$$M\cdot S + M'\cdot H_2 \rightarrow M' + S\cdot H_2 + M \quad (c)$$

According to scheme III, the complex activates hydrogen and the substrate separately, and in the general case the activation of these reagents may be brought about by different complexes. Examples of reactions of this kind are provided by various reactions of enzymatic catalysis, in which the substrate and hydrogen are activated by different centres[237].

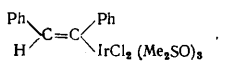
Activation of the substrate has been studied in most detail for the homogeneous hydrogenation of alkenes and alkynes. A theory of complex formation by alkenes and alkynes with transition metal compounds was put forward in 1952 by Dewar. A fairly large number of alkene and alkyne complexes have now been described, and a number of interesting reviews[238,239] have been devoted to these compounds. There is no doubt that the formation of a complex with the substrate is not sufficient for catalytic hydrogenation, which also requires that the bond between the substrate and the transition metal be fairly labile. Homogeneous hydrogenation is usually undergone only by those alkenes which react reversibly with the transition metal compound in solution[193]. Attempts to correlate the tendency of alkenes to undergo hydrogenation with the stability constants of the complex formed by the transition metal with these alkenes are extremely interesting in this connection[193,240]. According to the data of Osborn and coworkers[193], the equilibrium constant for the reaction of propene with the rhodium complex $RhCl(Ph_3P)_3$ is smaller by a factor of 2000 than that for ethylene, so that propene, unlike ethylene, is hydrogenated by means of this catalyst. The higher activity of $RhBr(Ph_3P)_3$ and $RhI(Ph_3P)_3$ compared with the corresponding chloride is in agreement with the lower stability of the complexes formed by the alkenes with the iodide and the bromide. The analogous complexes of rhodium with Ph_3As form more stable complexes with the alkene and are correspondingly less effective hydrogenation catalysts.

In the stage involving activation of the alkenes and acetylenes, both π- and σ-complexes with transition metal compounds may be formed. The hydride formed by the reaction of hydrogen with the transition metal compound according to scheme I (or introduced directly into the reaction mixture) may give a π-complex with the alkene (or alkyne), which is then converted into a σ-complex. This scheme was adopted, for example, by Jardine and McQuillin[196].

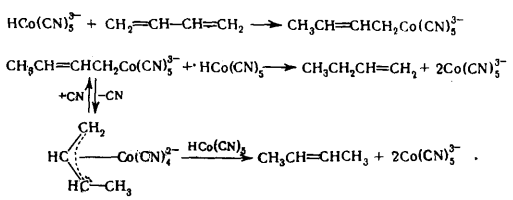
$$(Ph_3P)_3RuHCl + RC\equiv CR \rightarrow (Ph_3P_3)Ru\begin{matrix}H\\ \vdots\\ Cl\end{matrix}\cdots\begin{matrix}C\\ \|\\ C\end{matrix}\begin{matrix}R\\ \\ R\end{matrix} \rightarrow (Ph_3P)_3RuCR=CHR.$$

Examples of complexes containing both hydrogen and a π-bonded alkene on the same metallic centre are provided by the recently prepared complexes of iridium[241] $Ir_2HCl_2(C_8H_{12})_2$ and rhodium[242] $RhH_2(C_2H_4)(Ph_3P)_3$.

The organometallic σ-compound of iridium whose existence was assumed in the above scheme of Jardine and McQuillin was recently prepared[243]:

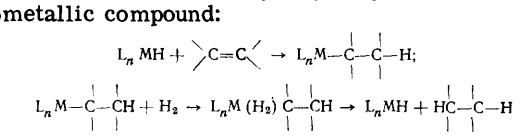


On acidification, this compound gives *cis*-stilbene. On the other hand, the reaction of the hydride with the substrate may involve the initial formation of a σ-complex, which is subsequently converted into a π-complex. Thus the following scheme was proposed to explain isomerisation during hydrogenation[119]:



The organometallic σ-compound formed may subsequently react with the transition metal hydride or undergo hydrogenolysis or hydrolysis (alcoholysis), depending on the conditions of the reaction. The hydrogenolysis of metal–carbon bonds is a fairly common phenomenon. Gilman[244] described the splitting of alkali metal compounds by hydrogen; Clauss and Bestain[245] described organometallic compounds of Mn and Ti, and Hein and Weiss[246,247] described compounds of chromium (the formation and properties of these derivatives have been reviewed[248,249]).

In a sense, the hydrogenolysis of a metal–carbon bond represents the activation of hydrogen by an intermediate organometallic compound:



A hydrogenation mechanism involving the formation of σ-alkyl complexes was assumed by Vaska[185] for an iridium complex, and has also been proposed for Ziegler–Natta catalysts[141,147], etc.

Although the formation of a σ-alkyl bond is widely encountered, this stage cannot always be observed in homogeneous hydrogenation. Thus in the hydrogenation of alkenes by means of a rhodium hydride, Osborn and coworkers[193], using the NMR method, were unable to detect the formation of a σ-C–Rh bond. In this instance, on the basis of the available experimental data, they put forward a hydrogenation scheme involving the simultaneous transfer of two hydrogens to the alkene.

The form in which the hydrogen is transferred to the compound being hydrogenated—ionic (see for example the review on hydride displacements[250]) or radical—depends to a large extent on the nature of the transition metal hydride, the substrate, the presence of a hydrogen carrier, the participation of the solvent, and other factors.

There is also the interesting possibility of carrying out catalytic hydrogenation without hydrogen transfer, by a mechanism involving electron transfer[251] (in this instance the solvent is the source of hydrogen):

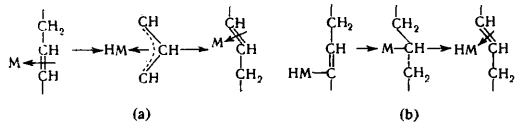
$$L_nM^{+m} + S \rightarrow L_nM^{+m+1}S^-$$
$$L_nM^{+m+1}S^- + H^+ \text{ (from solvent)} \rightarrow L_nM^{+m+1} + SH$$
$$L_nM^{+m+1} + H_2 \rightarrow L_nM^{+m} + 2H^+ \text{ etc.}$$

In most of the hydrogenating systems examined above, the activation of both hydrogen and the substrate was brought about by reaction with the same catalyst.

Complexes capable of activating hydrogen, however, are often not capable of simultaneously activating various substrates. On the other hand, the introduction, into a system containing a hydrogen activator, of substances capable of activating the substrate may extend considerably the range of application of the catalytic system. Khidekel'[229] points out that this method of activating the substrate differs fundamentally from the method of increasing the rate and specificity of homogeneous catalytic hydrogenation by modification of a catalyst activating molecular hydrogen. Thus organic compounds with carbonyl groups are not hydrogenated in the presence of the complex $RhCl(Ph_3P)_3$, which activates hydrogen. By adding zinc chloride, which forms complexes with carbonyl compounds, to the reaction mixture, however, Khidekel'[229] was able to hydrogenate carbonyl compounds under the same conditions.

4. ISOMERISATION OF THE SUBSTRATE DURING HOMOGENEOUS HYDROGENATION. THE SELECTIVITY AND STEREOSPECIFICITY OF HYDROGENATION CATALYSTS

Hydrogenation may be accompanied by a number of side reactions, depending on the nature of the substrate and the complex. One such reaction involving a transition metal hydride is the isomerisation of alkenes, described by many workers for complexes of Ir, Pt, Pd, Co, Ru, and Fe. It is now usual to consider "hydrido-σ-allyl" (a) and "hydrido-alkyl" (b) mechanisms of isomerisation, which can be represented schematically as follows[252-254]:



(a) (b)

Study of the distribution of isomers may give valuable information on the mechanism of homogeneous hydrogenation, since these processes involve the participation of a transition metal hydride with transfer of hydrogen by an "alkyl" or "allyl" mechanism. Work on the isomerisation of pent-1-ene in the presence of hydrogenation catalysts with a Pt–Sn bond is of interest in this connection[255].

In a number of instances, catalysts of homogeneous hydrogenation are extremely selective. Thus $LiAlH_4$ catalyses the homogeneous hydrogenation of pent-2-yne with the exclusive formation of pent-2-ene, and with conjugated alkenes, one C=C bond is preserved[41]; in the presence of the complex $Cp_2Ti(CO)_2$, hex-1-yne is hydrogenated to hex-1-ene[183]; the hydrogenation of sorbic acid by means of $[Co(CN)_5]^{3-}$ gives chiefly 2-hexenoic acid (see Table 1). The complex $Co_2(CO)_8$ can catalyse the hydrogenation of unsaturated aldehydes to saturated aldehydes, but at elevated temperature aliphatic aldehydes are hydrogenated to the corresponding alcohols. This property of the catalyst is extremely important for the control of hydroformylation. An important feature is that many catalysts of homogeneous hydrogenation, for example Ziegler–Natta systems[141] or the complex $RhCl(Ph_3P)_3$,[193] which are extremely active towards C=C and C≡C bonds, are incapable of reducing functional groups such as =CO, –CHO, –CN, –N=N–, $-NO_2$, etc.

Catalysts of homogeneous hydrogenation in a number of instances also show distinct stereospecificity. Thus in the hydrogenation of maleic acid by molecular deuterium in the presence of the complex $RhCl(Ph_3P)_3$, preferential cis-attachment of D_2 is observed, and the chief product is 1,2-dideuterosuccinic acid[193]. According to the observations of these authors, the quantity of *cis*-hex-2-ene obtained in the hydrogenation of hex-2-yne is twenty times the quantity of *trans*-hex-2-ene obtained.

The direction of hydrogenation sometimes depends on the conditions of the reaction. For example, the hydrogenation of butadiene by means of the $CoCl_2$–KCN system gives *trans*-but-2-ene at $CN^-/Co^{2+} \leqslant 5$, whereas but-1-ene is formed preferentially at $CN^-/Co^{2+} \geqslant 6$.[119]

V. ENZYMATIC CATALYSIS OF HYDROGENATION AND THE ISOTOPIC EXCHANGE AND CONVERSION OF HYDROGEN

Work by Stephenson, Strickland, and Green[256-259] laid the foundation for the study of a large class of micro-organisms capable of activating molecular hydrogen. This ability was ascribed to an enzyme or system of enzymes, named hydrogenase[260]. In the study of the catalytic power of hydrogenase, use is made of both the exchange and conversion of hydrogen[237,261-269] and hydrogenation[263-275].

Krasna and Rittenberg[264], on the basis of a study of the kinetics of these reactions, proposed the mechanism $H_2 + E \rightleftharpoons H:E^- + H^+$, where E represents hydrogenase, and the HE^- formed takes part in hydrogenation or the exchange or conversion of hydrogen.

When Methylene Blue or hexacyanoferrate(III) is added to an aqueous suspension of *Pr. vulgaris*, D_2–H_2O exchange is inhibited, and the rate of exchange increases to its previous value only after an induction period, during which hydrogenation of the substrate takes place[265,267]. In the opinion of the authors cited, this shows that the same intermediate compound is formed during hydrogenation and exchange.

The same opinion is held by Farkas and Fisher[237], who studied the hydrogenation of fumarate in the presence of inhibitors of two types (CN and urethane).

Peck and coworkers[266] cast doubt on the idea that the catalysis of isotopic exchange by hydrogenase is a necessary condition for hydrogenating power in hydrogenase, since the rate of exchange in the presence of *Az. vin.*[276,277] and *Rhod. rubrum*[278] is very low compared with the rate of hydrogenation. Study of the catalytic activity of a wide range of micro-organisms showed that the rate of reduction of Methylene Blue is also increased by enzymes which have no significant catalytic effect on exchange. The authors cited emphasise that these results do not agree with the mechanism of Krasna and Rittenberg[264], and they put forward a reaction scheme, according to which hydrogen is activated by an iron-containing enzyme; the reduced enzyme can be oxidised by Methylene Blue or by

other acceptors, with the participation of a flavine component:

$$H_2 + E(Fe^{3+}) \rightleftarrows E(Fe^{2+}) : 2H$$
$$\downarrow \text{flavine}$$
$$\text{Methylene Blue}$$

They do not, however, exclude an alternative mechanism, according to which a complex of the reduced enzyme may combine with flavine and be oxidised by one-electron acceptors such as viologen dyes, the reaction involving a second metal atom as a functional component of the hydrogenase:

$$E(Fe^{2+})\ \text{flavine} : 2H \xrightarrow{Mo} 2\ \text{viologen} \cdot \bar{e} + 2H^+$$

The presence of iron in hydrogenase was established by Hoberman and Rittenberg[263], Peck and coworkers[266], and Gest[272]; Peck and coworkers[266] also discuss the part played by Mo.

The activation of hydrogen according to the scheme proposed by Rittenberg and Krasna is heterolytic[3]:

$$\overline{Fe^{3+}} + : B \rightleftarrows \overline{FeH^+} + H : B^+$$

whereas according to Gest and coworkers it is homolytic, the rupture of the H–H bond taking place on two metallic centres.

In heterolytic rupture of H_2, the reduction of two-electron acceptors such as Methylene Blue becomes possible, whereas one-electron processes, such as the reduction of viologen dyes and D_2–H_2O exchange, require the participation of a second metal. This explains the observation that *Az. vin.* and *Rhod. rubrum* catalyse the reduction of Methylene Blue but do not catalyse exchange.

The main features of the results obtained by Krasna and Rittenberg[265,267] in the study of the catalytic activities of various micro-organisms agree with those obtained by Peck and coworkers[266]. They found, however, that exchange is observed in all instances when reduction of Methylene Blue takes place.

Comparison of the hydrogenating power of the bacterium *Ph. vulgaris* with the activity of $[Co(CN)_5]^{3-}$ led King and Winfield[137] to the conclusion that the mechanisms of hydrogenation by hydrogenase and pentacyanocobaltate are the same.

The activation energy for D_2–H_2O exchange by means of the bacterium *Pr. vulgaris* suspended in a phosphate buffer is 7.7 kcal mole^{-1};[263] other authors give the value 14 kcal mole^{-1}.[237] Couper and coworkers[269] determined the activation energy for the exchange and conversion of hydrogen, catalysed by *Pr. vulgaris* and *E. coli*. According to their data, for *Pr. vulgaris*, the activation energy for $D_2 + H_2O$ exchange is 7.47 ± 1.11 kcal mole^{-1}, and that for the ortho-para conversion of hydrogen 7.35 ± 0.46 kcal mole^{-1}.

Thus the enzymatic catalysis of hydrogenation by means of hydrogenase involves an extremely complicated chain of catalytic processes, responsible for the exceptional activity and stereospecificity of the processes under mild conditions. In this connection, the study of transition metal compounds as catalysts of homogeneous hydrogenation gives extensive material for constructing models of biochemical processes. An exceptionally important feature is the presence of a transition metal in hydrogenase. The part played by cobalamin (an enzyme containing Co[279-281]) in hydrogen transfer is extremely important. One example of the construction of a model of this enzyme is the use of cobaloxime—a model of vitamin B_{12S}—as hydrogen carrier in a system containing a rhodium catalyst which brings about the homogeneous activation of molecular hydrogen[282].

It can confidently be stated that the study of the mechanism of action of enzymatic systems is giving valuable information for the creation of new and effective complex catalysts for homogeneous hydrogenation. The introduction, into catalytic systems, of hydrogen carriers and additives capable of activating the substrate, together with modification of the hydrogen activation catalysts themselves, is now making it possible to obtain highly effective hydrogenation catalysts.

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The number of known systems capable of activating hydrogen under the conditions of a homogeneous reaction—Lewis bases and acids, salts and complexes of transition metals—is now extremely large. Among compounds of these classes, the transition metal complexes show the greatest activity.

The catalytic action of transition metal complexes is observed under comparatively mild reaction conditions, and their activity in the hydrogenation of organic compounds in a number of instances is as high as or even greater than that of heterogeneous catalysts. An understanding of the mechanism of action of homogeneous hydrogenation catalysts is of assistance in the investigation of the mechanism of heterogeneous catalytic hydrogenation and also the mechanisms of polymerisation, hydroformylation, and other reactions.

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Institute of Organoelemental Compounds,
Academy of Sciences of the USSR,
Moscow

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Electron Spin Resonance Spectra, Conformation, and Chemical Properties of Free Radicals in Solid Polymers

P.Yu.Butyagin, A.M.Dubinskaya, and V.A.Radtsig

The structure and the chemical properties of polymeric radicals having their free valency on a carbon atom in the main chain are surveyed. Most of the information on radicals in solid polymers has been obtained by electron spin resonance. The first part of the review gives a detailed analysis of the hyperfine structure of the e.s.r. spectra, which is closely related to the structure and the conformation of the radicals. The second part deals with the chemical behaviour of polymeric radicals in solid matrices at low temperatures (80-300°K). All the data relate to radicals from polymers of the vinyl series, polyoxides, and polyamides. A list of 112 references is given.

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I. INTRODUCTION

In the vinyl series of polymers, radicals having their free valency on carbon atoms of the main chain can have the structures

$$\underset{(I)}{-CXY-\dot{C}H_2} \quad \underset{(II)}{-CH_2-\dot{C}XY} \quad \underset{(III)}{-CH_2-\dot{C}X-CH_2-} \quad \underset{(IV)}{-CXY-\dot{C}H-CXY-}$$

where X = H, CH_3, C_6H_5, OH, $COOCH_3$, $OCOCH_3$, CN, etc. and Y = H, CH_3, etc. The radicals (I)-(IV) are formed in polymers by the action of ionising radiation, ultraviolet irradiation, exposure to a laser beam, mechanically, thermally, chemically, and also during polymerisation of the monomers.

Action of Ionising Radiation

The action of X-rays, γ-rays, fast electrons, ultraviolet radiation, etc. on a polymer chain most often detaches a light atom (hydrogen) or a group of atoms, with the formation of radicals (III) or (IV). These have been detected and examined by e.s.r. in polyethylene[1,2], polyamides[3,4], polyisobutylene[5,6], poly(vinyl alcohol)[7], and other polymers. In individual cases, e.g. in the γ-irradiation[8,9] and the photolysis[10] of polyacrylate polymers, radicals of type (II) are observed.

Mechanical Treatments

Bonds in the main chain of various heterochain and carbon-chain polymers are ruptured by cutting[11-13], grinding[14-16], stretching fibres[17,18], and other types of destruction and deformation of specimens. Radicals (I) and (II) are the primary degradation products. In polyethylene[19,20], polypropylene[19], poly(vinyl alcohol)[21], polystyrene[22], and other polymers both terminal radicals have been recorded during the mechanical degradation of macromolecules distributed in a matrix of an inert substance (method of dispersion of frozen dilute solutions of polymers[21,23]). In polyethylene[19], poly(methyl methacrylate)[13], polyamides[20], polyformaldehyde[21], and several other polymers the active primary radicals are converted by secondary reactions into radicals having the free valency in the middle of the chain.

Polymerisation of Monomers

Terminal radicals of only one type, $-CH_2-\dot{C}XY$ (or $-CH_2-\dot{C}HX$), are observed in all cases in the polymerisation of monomers. In the liquid phase the steady-state concentration is usually low (10^{-9} M), and the radicals have been detected only by the initiation of polymerisation by means of redox systems directly in the resonator of a highly sensitive e.s.r. spectrometer[24-27]. Well resolved e.s.r. spectra of a large number of radicals have been obtained by this method. It is considerably easier to observe radicals at the gelatinisation stage[28], in the polymerisation of monomers which undergo cross-linking[29,30], during heterogeneous polymerisation, when the polymer is precipitated[31,32], and also in solid-phase polymerisation initiated by γ-rays or ultraviolet irradiation of the monomers[31,33-36].

Action of Atomic Hydrogen

The action of atomic hydrogen and other simple radicals on macromolecules provides a convenient chemical method for initiating polymer radicals. The hydrogen atoms are obtained by passing hydrogen over an incandescent tungsten filament[37], in a high-frequency discharge[38,39], by the photolysis of redox systems [e.g. frozen aqueous solutions of iron(II) sulphate plus sulphuric acid[40]], among other methods. The interaction of hydrogen atoms with molecules yields radicals either by addition (to the benzene ring in polystyrene[41], and to pyrimidine and purine bases in deoxyribonucleic acids[42]) or by detachment ($H + RH \rightarrow \rightarrow H_2 + R^{\cdot}$) at the site of a weak carbon-hydrogen bond.

Thus the structure of the primary radicals is determined by the type of action on the polymer: mechanical cleavage of macromolecules yields two terminal radicals; reactions with hydrogen atoms should produce radicals having the free valency in the middle of the chain or on lateral groups; polymerisation should involve the formation of $-CH_2-\dot{C}XY$ radicals; etc. Radiolysis, ultraviolet irradiation, and mechanical working are usually accompanied by secondary free-radical reactions, and the structure of the final radicals, which are stable under the given conditions, will depend in considerable measure on the nature, state, and properties of the polymer. Secondary

reactions can be inhibited by lowering the temperature, using inert matrices, or other methods.

In many cases the generation of radicals is accompanied by changes in the structure and the properties of the polymer chain: new functional groups appear, the molecular weight diminishes, cross-links are formed between molecules, the secondary structure of the polymer changes, etc. These changes must be taken into account in analysing the properties of the radicals and the kinetics of the secondary free-radical reactions.

II. ELECTRON SPIN RESONANCE SPECTRA AND CONFORMATION OF POLYMERIC RADICALS

The chief characteristic of the e.s.r. spectra of polymer radicals is their hyperfine structure. The number and position of the lines constituting this structure depend on the location of the free valency in the macromolecule and the conformation of the radical, the angle of rotation about the $C(\alpha)-C(\beta)$ bond. The hyperfine structure of the spectra of alkylated radicals results from interaction of the unpaired electron with the magnetic nuclei of the α- and β-hydrogen atoms:

$$\rangle C_{(\beta)}H-\dot{C}_{(\alpha)}H-\dot{C}_{(\beta)}H\ .$$

The hyperfine interaction with α-protons comprises two parts—isotropic and anisotropic—the latter depending on the orientation of the $C(\alpha)-H$ bond in the magnetic field[43]. The position of a line in the e.s.r. spectra of polycrystalline and amorphous specimens is determined solely by the isotropic portion of the hyperfine interaction, while the anisotropic part merely broadens the line[44]. With oriented specimens the anisotropy of the hyperfine interaction leads to a considerable shift in individual components of the spectrum[2,45]. Hyperfine interaction with β-protons is mainly isotropic.

It is as yet impossible to calculate theoretically the hyperfine interaction in complicated radicals, and analysis of the spectra is based on semi-empirical relations established[24,26,46-50] from the study of dozens of spectra. Quantitative estimates of the isotropic hyperfine interaction constants are founded on measurements of the e.s.r. spectra of radicals of low molecular weight in the liquid phase, where the hyperfine structure is well resolved and the positions of the lines are fixed with great accuracy.

1. Semi-empirical Rules for the Analysis of Electron Spin Resonance Spectra

The width of an e.s.r. spectrum—the distance between the extreme lines of the hyperfine structure—is given by the sum of the values for the splitting on all the α- and β-protons:

$$\Sigma a_H = \Sigma a_H(\alpha) + \sum_i a_H(\beta_i)\ . \qquad (1)$$

According to McConnell[47] the spectroscopic splitting constant $a_H(\alpha)$ for each α-proton is given by

$$a_H(\alpha) = Q_\alpha \cdot \rho \qquad (2)$$

where ρ is the spin density of the unpaired electron on the α-carbon atom, and Q_α a coefficient of proportionality, whose value depends on the nature of the bonds and the type of substituents.

In substituted alkyl radicals the density of the unpaired electron on the α-carbon atom is determined by the nature of the substituents[46,49]. In radicals of the type

$$X-\dot{C}(Z)-Y$$

the value of ρ can be calculated by means of the formula

$$\rho = (1-\Delta X)(1-\Delta Y)(1-\Delta Z)\ . \qquad (3)$$

The quantity ΔX indicates the fraction of the spin density which the substituent X attracts to itself, it being assumed that each substituent behaves independently of the others. Table 1 gives the values of ΔX for various functional groups, all calculated from experimental data[46,49]. For the methyl groups theoretical calculations have also been made[51]. For the hydrogen atom $\Delta H = 0$, and the decrease in spin density for alkyl substituents and groups of the types CH_2R and COOR does not exceed 10%. The "strongest" substituents are the carbonyl, ether, and hydroxyl groups, where the diminution in density reaches 15–18%.

Table 1. Values of the parameter $\Delta(X)$ for various substituents in alkyl radicals[46,49].

X	Δ(X)	X	Δ(X)
—H	0.000	—COOR	0.072
$-CH_3$	0.081	—OCHO	0.136
$-C_2H_5$	0.082	$-OCH_2CH_3$	0.180
$-CH_2CH_2OH$	0.092	—OH	0.160
$-CH_2OH$	0.079	—CN	0.148
$-CH_2COOR$	0.080	$-C_6H_5$	0.290*
$-CH_2NH_2$	0.034	$-[CH_2-C(CH_3)(COOH)]_n$	0.101
—CH(OH)COOH	0.041	$-[CH_2-CH(COOH)]_n$	0.050
$-C(C_6H_5)_3$	0.044		

*For the radicals $C_6H_5\dot{C}(CH_3)_2$ of isopropylbenzene $a_H(CH_3) = 17.5$ oersteds. Hence according to Eqns. (3) and (11) $\rho = 17.5/29.3 \simeq 0.6$ and $\Delta(C_6H_5) \simeq 0.290$.

Table 2 gives values of the parameter Q_α for α-protons in alkyl and alkylated radicals. When the substituent X is bound to the α-carbon atom by a C–C bond (CH_2R, COOH, etc.), the values usually fluctuate within the limits $Q_\alpha = 24.1 \pm 0.7$ oersteds. The alkyl radicals $R_1\dot{C}HR_2$ (where $R = CH_3$, C_2H_5, etc.) form an exception, Q_α being rather larger. For radicals in which the substituent is bound to the α-carbon atom by a C–O bond, the parameter Q_α is almost 5 oersteds smaller: $Q_\alpha = 19.4 \pm 1.0$ oersteds.

The hyperfine structure constant for β-protons depends on the conformation of the radical[48]—the angle of rotation about the $C(\alpha)-C(\beta)$ bond:

$$a_H(\beta) = Q_\beta \cdot \rho \cdot \cos^2\theta, \qquad (4)$$

where Q_β is a constant whose value for alkylated radicals is 58.6 oersteds[24,26], and θ is the angle between the axis of the $2p_z$-orbital of the unpaired electron and the projection of the $C(\beta)-H$ bond on a plane perpendicular to the $C(\alpha)-C(\beta)$ bond (Fig. 1).

The relation (4) is valid provided the amplitude of oscillations of the $C(\alpha)-C(\beta)$ bond about the equilibrium position θ_0 is small. With large amplitudes (tens of degrees) we must replace $\cos^2\theta$ in Eqn. (4) by the value

$\langle\cos^2\theta\rangle$,[57] averaged over the internal motions in the radical (vibrations or rotation). The averaged value is connected with the equilibrium value by the formula

$$\langle\cos^2\theta\rangle = A + B\cos^2\theta_0 \qquad (5)$$

where A and B depend on the temperature and the form of the potential curve for the internal motions in the radical. As $T \to 0$, we have $A \to 0$ and $B \to 1$.

Table 2. Value of the parameter $Q(\alpha)$ for X–$\dot{C}$H–Y radicals (calculated from data of Refs. 24, 26, 46, 52–55).

X	Y: –H	Y: –CH_3, –CH_2CH_3	Y: –CH_2NH_2, –CH_2OH
–H	23.0	24.2±0.2	—
–CH_3	—	26.1±0.1	—
–CHR_1R_2 (R=H, CH_3OH, COOH, NH_2)	—	24.9±0.1	—
–COOR (R=H, CH_3, C_2H_5)	23.5	23.7±0.2	23.9±0.3
–COR (R=CH_3, C_2H_5)	24.2	23.6(?)	24.6
–CN	25.4(?)	25.4	25.3±0.3
–OH	20.9±0.4	20.4±0.4	22.3
–OR (R=C_2H_5, CHO)	—	18.1±0.6	—
–C_6H_5	23.2*	—	—

*Value obtained from $a_H(\alpha)$ = 16.4 oersteds for the benzyl radical[56].

In polymer radicals in the solid phase at low temperatures, movements in the radicals are usually strongly retarded, and Eqn. (4) can perfectly well be used for analysing the hyperfine structure of the e.s.r. spectra. Equation (5) must be employed to investigate the temperature dependence of the splitting on the β-protons.

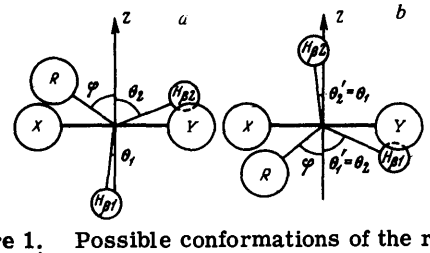


Figure 1. Possible conformations of the radical R–CH_2–$\dot{C}$XY.

The influence of the conformation of the radicals on the form of the e.s.r. spectra is best seen from the example of radicals have a β-methylene group

$$R-CH_2-\dot{C}(Y)-X.$$

In Fig. 1 the carbon atom C is located in the plane of the paper, the thick lines indicate the projections of the $C_{(\alpha)}$–X and $C_{(\alpha)}$–Y bonds, while the ordinary lines represent $C_{(\beta)}$–H and $C_{(\beta)}$–R bonds. The Z-axis is the axis of the orbital of the unpaired electron. The angle φ, where (see Fig. 1)

$$\theta_1 = \frac{\pi}{3} + \varphi, \quad \theta_2 = \frac{\pi}{3} - \varphi, \qquad (6)$$

characterises the conformation of the radical.

The two equilibrium positions (a) and (b) are energetically equivalent. The lifetime of the radical in each of these positions is

$$\tau = \tau_0 \exp\left(\frac{E}{RT}\right) \qquad (7)$$

where τ_0 is the period of the oscillations and E the height of the potential barrier which must be overcome for transition from one conformation to the other. The number of components of the hyperfine structure in the e.s.r. spectrum depends on the relation between the frequency of the conformational transitions and the quantity $\nu_a - \nu_b$,[58] in which ν_a and ν_b are the frequencies of hyperfine interaction for β-protons in conformations (a) and (b). This difference $\nu_a - \nu_b$ is usually close to 10^7–10^8 s^{-1}. Three cases are possible.

With a high barrier at low temperatures, $\tau \gg (\nu_a - \nu_b)^{-1}$, and the e.s.r. spectrum consists of the sum of the signals corresponding to conformations (a) and (b) (the β-protons are non-equivalent). Then

$$a_H(\beta\text{-}1) = Q_\beta \cdot \rho\cos^2\left(\frac{\pi}{3} + \varphi\right) \text{ and } a_H(\beta\text{-}2) = Q_\beta \cdot \rho\cos^2\left(\frac{\pi}{3} - \varphi\right). \qquad (8)$$

The constants $a_H(\beta\text{-}1)$ and $a_H(\beta\text{-}2)$ are interrelated. In Fig. 2 the ordinates represent $f_1 = \cos^2(\frac{1}{3}\pi + \varphi)$ and $f_2 = \cos^2(\frac{1}{3}\pi - \varphi)$, while the abscissae are the conformational angles φ. When $\varphi = 0$ and 90° the splitting is the same on the two β-protons. Over the range $20° < \varphi < 40°$ the splitting on one of the β-protons is small, and is hardly observable in poorly resolved e.s.r. spectra of polymer radicals.

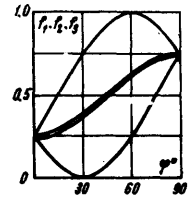


Figure 2. Graphs of the functions

$$f_1 = \cos^2\left(\frac{\pi}{3} + \varphi\right),$$

$$f_2 = \cos^2\left(\frac{\pi}{3} - \varphi\right)$$

and

$$f_3 = \tfrac{1}{2}\left[\cos^2\left(\frac{\pi}{3} + \varphi\right) + \cos^2\left(\frac{\pi}{3} - \varphi\right)\right]$$

(double line).

Rapid alternation of conformations results in an averaging of the hyperfine interaction constants, and when $\nu \ll (\nu_a - \nu_b)^{-1}$ the β-protons are equivalent:

$$a_H(\beta\text{-}1) = a_H(\beta\text{-}2) = \tfrac{1}{2}Q_\beta \cdot \rho\left[\cos^2\left(\frac{\pi}{3} + \varphi\right) + \cos^2\left(\frac{\pi}{3} - \varphi\right)\right]. \qquad (9)$$

The dependence of $f_3 = \frac{1}{2}[\cos^2(\frac{1}{3}\pi + \varphi) + \cos^2(\frac{1}{3}\pi - \varphi)]$ on φ for this case is shown by the double line in Fig. 2. The splitting is a maximum at $\varphi = 90°$.

In the intermediate case, when the frequency of interchange is comparable with the frequency of conformational transitions, i.e. $\tau \simeq (\nu_a - \nu_b)^{-1}$, exchange broadening of the central lines of the spectrum will be observed. This comparatively rare case has been examined in detail[24,46].

From Eqns. (8) and (9) it is seen that the total splitting on the β-protons is independent of the frequency of the transitions, being determined solely by the conformation of the radical. We always have

$$a_H(\beta\text{-}1) + a_H(\beta\text{-}2) = Q_\beta \cdot \rho \left[\cos^2\left(\frac{\pi}{3} + \varphi\right) + \cos^2\left(\frac{\pi}{3} - \varphi\right)\right] . \quad (10)$$

Calculation of the hyperfine interaction constants is considerably simplified for the radicals

$$CH_3-\dot{C}(Y)-X$$

containing a β-methyl group, since even at low temperatures the methyl groups rotate about the $C_{(\alpha)}-C_{(\beta)}$ bond at a frequency exceeding that of the hyperfine interaction (free rotation[46,59]), and all three β-protons are equivalent. With free rotation

$$\cos^2\theta = {}^1/_2\pi \int_0^{2\pi} \cos^2\theta d\theta = {}^1/_2 \text{ and } a_H(CH_3) = {}^1/_2 Q_\beta \rho = 29.3\rho . \quad (11)$$

Thus, in the analysis of the e.s.r. spectra of alkylated radicals, the hyperfine structure constants for α-protons and the protons of β-methyl groups can be estimated to ~ 5% from Eqns. (2), (3), and (11) and Tables 1 and 2. With $a_H(\alpha)$ and $a_H(CH_3)$ known, the total width of the spectrum depends solely on the splitting on the β-protons, of CH_2R or CHR_1R_2 groups, i.e. on the angle of rotation about the $C(\alpha)-C(\beta)$ bond. Consequently the conformation of the radical can be determined when the total width of the spectrum is known; and conversely, if the conformation is known, the position of all the lines in the spectrum can be predicted.

Actual examples of the analysis of e.s.r. spectra of polymer radicals belonging to various types will be examined in the following section.

2. Electron Spin Resonance Spectra of the Main Types of Polymer Radicals

Data on the e.s.r. spectra at 77°K of polymer radicals having the free valency at the ends and in the middle of the chain are assembled in Figs. 3–5. In most cases we have determined the values of ρ, Q, a_H, and φ from an analysis of the e.s.r. spectra published by various authors; the hyperfine structures were analysed according to the rules formulated in the preceding Section. Individual spectra and the corresponding schemes of energy levels are shown in Figs. 3 and 4. In most cases there is no doubt about the reliability of the interpretation of the spectra, which either is proved by direct methods (investigation of oriented specimens[2,4,60], deuteriated radicals[3,61], etc.) or is supported by many indirect data, from the method of preparing the radicals to analysis of the expected conformation.

In compiling the tables the hyperfine structure constants for α-protons $a_H(\alpha)$ and the protons of methyl groups $a_H(CH_3)$ were calculated by means of Eqns. (2) and (11). Values of ρ were estimated by means of Eqn. (3) with the data in Table 1 taken into account; the electron density drawn off by the polymer chain was taken to be 0.08. The constant Q_α was determined from Table 2. The splitting on β-protons of CHX and CH_2 groups was found as the difference between the total width of the spectrum† and the value of the expression $\Sigma a_H(\alpha) + \Sigma a_H(CH_3)$. The ratios between $a_H(\beta\text{-}1)$ and $a_H(\beta\text{-}2)$ and the conformational angle φ were determined from the graph in Fig. 2.

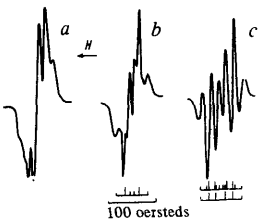


Figure 3. Electron spin resonance spectra of terminal radicals (at 80°K) in: *a*, *b*) poly(vinyl alcohol); *c*) polyethylene.

(*a*) R–$\dot{C}H_2$ radicals

Terminal CXY–$\dot{C}H_2$ radicals are distinguished by high chemical activity in reactions involving transfer of the free valency (see Section III, 1), so that it is very difficult to isolate and investigate them. Radicals of type (I) have been fixed by the low-temperature mechanical degradation of polymers (linear polyethylene[19,20], polycaprolactam[20]), by the dispersion of frozen dilute solutions of poly(vinyl alcohol)[21], polystyrene[22], and certain other polymers, and by the radiolysis of polyformaldehyde[60].

Radicals CXY–$\dot{C}H_2$ are formed together with radicals of other types (II) and (III), and the e.s.r. spectra are usually the result of the superposition of two or three signals. As a rule, however, lines belonging to radicals of type (I) are less easily saturated than are the remaining signals. This facilitates the isolation and interpretation of the spectra of CXY–$\dot{C}H_2$ radicals (Table 3). However, the accuracy with which the hyperfine interaction constants are determined remains low (1–3 oersteds).

Fig. 3 shows as example the spectra (*a*) and (*b*) of free radicals formed at the site of cleavage of the polymer chain of poly(vinyl alcohol) (1% frozen solution in D_2O after dispersion in a vacuum at 90°K). The spectrum 3*a* corresponds to a low microwave power and 3*b* to a high microwave power (~ 0.5 and ~ 50 mV respectively). With a low power the lines of the $CH(OH)\dot{C}H_2$ and $CH_2\dot{C}H(OH)$ signals make roughly the same contribution to the overall spectrum, whereas at high microwave powers the signal due to the latter radicals is saturated, and the symmetrical spectrum of CH(OH)–$\dot{C}H_2$ radicals predominates (Fig. 3*b*). The width of the latter is 80 oersteds, and the splitting on each α-proton is $a_H(\alpha) = Q_\alpha\rho = 24.4 \times 1 \times 1 \times (1 - 0.08) = 22$ oersteds. Hence $a_H(\beta) = 80 - 2 \times 22 = 36$ oersteds. The set of levels of the hyperfine structure is shown below the spectrum.

† The total width of the spectrum was determined with the finite width of individual components allowed for[62].

The e.s.r. spectrum of the terminal radicals $CH_2-\dot{C}H_2$ is obtained by the mechanical disintegration of linear polyethylene in an inert atmosphere at 80°K.[19,20] The total width of the spectrum[20] is 115 oersteds, while $a_H(\alpha) = 22$ oersteds, and the splitting on the β-protons is $a_H(\beta\text{-}1) + a_H(\beta\text{-}2) = \Sigma a_H - 2a_H(\alpha) = 115 - 2 \times 22 = 71$ oersteds. Hence with $Q_\beta = 58.6$ and $\rho = 0.92$, we have

$$\frac{^1/_2\,[a_H(\beta\text{-}1) + a_H(\beta\text{-}2)]}{58.6 \cdot 0.92} = 0.66.$$

In Fig. 2 the ordinate 0.66 intersects the double line of the graph at the conformational angle $\varphi = 68°$. With non-equivalent β-protons and $\varphi = 68°$, we have $a_H(\beta\text{-}1) = 53$ oersteds and $a_H(\beta\text{-}2) = 18$ oersteds. The upper set of hyperfine structural levels below the spectrum 3*c* corresponds to these values. The actual splittings on the β-protons, 50 and 21 oersteds respectively, differ by ±3 oersteds from the calculated values (see lower scheme in Fig. 3*c*). The difference may be due to strong internal motion about the $C(\alpha)-C(\beta)$ bond. The barrier to rotation in the $CH_2-\dot{C}H_2$ radical is probably low, and the exact equation (5) should be used instead of the approximate formula (4) for a rigorous calculation of $a_H(\beta)$.

In $CHX-\dot{C}H_2$ and CH_2-CH_2 radicals, in contrast to $\rangle C-CH_3$ radicals, there is no free rotation about the $C(\alpha)-C(\beta)$ bond, and the conformational angle φ depends on the nature of the substituent X (see Table 3). With radicals containing a single β-proton, the same value of $a_H(\beta)$ may correspond to two different conformations (the angles φ_1 and φ_2, where $\varphi_1 + \varphi_2 = 2\pi/3$). Table 3 gives only the angle φ_1.

Table 3. Parameters of e.s.r. spectra of $R-\dot{C}H_2$ radicals (at 80°K).

Polymer radical	Σa_H, oersteds	ρ	Q_α	$a_H(\alpha)$, oersteds	$a_H(\beta\text{-}1)$, oersteds	$a_H(\beta\text{-}2)$, oersteds	$\varphi°$	Preparation of radical*	Ref.
$-CH_2-\dot{C}H_2$ Polyethylene, polycaprolactam	115	0.92	24.4	22	53	18	68	M*	19, 20
$-CH(OH)-\dot{C}H_2$ Poly(vinyl alcohol)	80	0.92	24.4	22	36	—	25	M	21
$-CH(C_6H_5)-\dot{C}H_2$ Polystyrene	77	0.92	24.4	22	33	—	21	M	22
$-O-\dot{C}H_2$ Polyformaldehyde	36	0.84	18.4	18	—	—	—	R	5,60
$-CH(OCOCH_3)-\dot{C}H_2$ Poly(vinyl acetate)	81	0.92	24.4	22	37	—	26	M	22
$-CH(COOCH_3)-\dot{C}H_2$ Poly(methyl acrylate)	84	0.92	24.4	22	40	—	30	M	22
$-NH-\dot{C}H_2$ Polycaprolactam	38	—	—	19	—	—	—	M	20

*In Tables 3–5 M = mechanical degradation, R = radiolysis, P = polymerisation, and UV = ultraviolet irradiation.

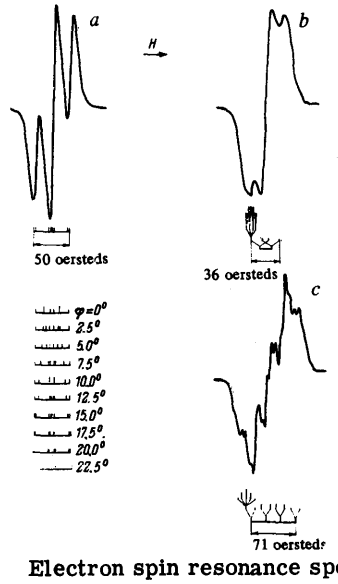


Figure 4. Electron spin resonance spectra and scheme of hyperfine levels for the radicals:
a) $-CH_2-\dot{C}H(COOCH_3)$, poly(methyl acrylate);
b) $-CH_2-\dot{C}H(C_6H_5)$, polystyrene;
c) $-CH_2-\dot{C}(CH_3)(C_6H_5)$, poly-$\alpha$-methylstyrene.

Table 4. Parameters of e.s.r. spectra of $CH_2-\dot{C}XY$ radicals (at 80°K).

Structure of radical	Form of spectrum: No. of hyperfine components	Form of spectrum: Σa_H, oersteds	ρ	Q_α, oersteds	$a_H(\alpha)$, oersteds	$a_H(CH_3)$, oersteds	$a_H(\beta\text{-}1)$, oersteds	$a_H(\beta\text{-}2)$, oersteds	φ	Production of radical	Ref.
$-CH_2-\dot{C}H(CH_3)$ Polypropylene	8	162	0.82	26.2	22	25	48	17	67	M	19
$-CH_2-\dot{C}H(COOCH_3)$ Poly(methyl acrylate)	3	46	0.85	23.5	20	—	25	3	15	M,R,P	11, 22, 33, 34
$-CH_2-\dot{C}H(COOH)$ 1)	3	46	0.85	23.5	20	—	25	3	16	M,P	11, 35
Polyacrylic acid 2)	5	46	0.85	23.5	20	—	14	11	3	R,P	9, 63
$-CH_2-\dot{C}H(C_6H_5)$ Polystyrene	3	36	0.65	23.2	15	—	21	2	17.	M,P	15, 63
$-CH_2-\dot{C}H(CN)$ Polyacrilonitrile	3	44	0.78	25.4	20	—	24	3	17	P	33
$-CH_2-\dot{C}(CH_3)_2$ Polyisobutene	15	162	0.78	—	—	23	11	13	2	M,P	6, 12
$-CH_2-\dot{C}(CH_3)(COOH)$ Polymethacrylic acid	9	92	0.78	—	—	22.5	14	11	3	M,R,P	9, 11, 50
$-CH_2-\dot{C}(CH_3)(COOCH_3)$ Poly(methyl methacrylate)	9	92	0.78	—	—	22.5	14	11	3	M,R,P	8–12, 28, 31, 33, 63 etc.
$-CH_2-\dot{C}(CH_3)(C_6H_5)$ Poly-α-methylstyrene	16	84	0.60	—	—	1) 17.5 2) 17.5	11 17	5 2	5 15	M,R	63
$-CH_2-\dot{C}(CH_3)(CN)$ Polymethacrylonitrile	9	86	0.72	—	—	21	11.5	11.5	0	R	31

(*b*) $CH_2-\dot{C}HX$ and $CH_2-\dot{C}(CH_3)X$ radicals

In most cases polymer radicals of type (II) can be obtained by the polymerisation of monomers in viscous and solid media. Hence there is no doubt that the e.s.r. spectra in Table 4 do actually belong to $CH_2-\dot{C}XY$ radicals.

Fig. 4*a* shows the spectrum of $CH_2-\dot{C}H(COOCH_3)$ radicals, which is a triplet of width 46 ± 1 oersteds. In this case $a_H(\alpha) = 23.5 \times 1 \times (1 - 0.08)(1 - 0.07) = 20$ oersteds. For the determination of $a_H(\beta\text{-}1)$ and $a_H(\beta\text{-}2)$ Fig. 4*a* shows a scheme of hyperfine levels corresponding to values of the angle φ from 0 to 22.5°. A triplet 46 oersteds wide can be obtained with $a_H(\beta\text{-}1) = 25$ oersteds and $a_H(\beta\text{-}2) = 3$ oersteds ($\varphi = 15°$).

The spectrum in poly-α-methylstyrene comprises 16 hyperfine components each separated by 5.5 oersteds (Fig. 4*c*), this splitting being due to interaction of the unpaired electron with the *ortho*- and *para*-protons of the benzene ring. A similar "aromatic" hyperfine structure has been observed in the spectra of the relatively simple radicals $C_6H_5\dot{C}H_2$, $C_6H_5\dot{C}H(CH_3)$, etc.[56,64] A 16-component spectrum of $CH_2-\dot{C}(CH_3)(C_6H_5)$ radicals can be obtained with two values of φ: when $\varphi = 6°$, we have $a_H(\beta\text{-}1) = 11$ and $a_H(\beta\text{-}2) = 5$ oersteds; the corresponding values with $\varphi = 15°$ are 17 and 2 oersteds. Choice of the correct alternative requires a knowledge of the relative intensities of the spectral lines: i.e. the spectrum in the liquid phase must be obtained.

No splitting on the protons of the benzene ring is detected in the spectrum of $CH_2-\dot{C}H(C_6H_5)$ radicals (Fig. 4*b*). In this case, perhaps, the "aromatic" hyperfine structure is obscured by the splitting of 3 oersteds on one of the β-protons of the methylene group.

Table 4 shows that $a_H(\beta\text{-}1) \neq a_H(\beta\text{-}2)$ for all radicals of type (II) at 77°K: i.e. the frequency of conformational transitions is low. In $CH_2-\dot{C}HX$ radicals other than $CH_2-\dot{C}H(CH_3)$ the angle of rotation about the $C(\alpha)-C(\beta)$ bond lies within the range $\varphi = 15-17°$: i.e. the nature of the substituent X (COOH, $COOCH_3$, C_6H_5, CN) has no great effect on the conformation of the radical. The conformation is also practically independent of X for all $CH_2-\dot{C}X(CH_3)$ radicals, the angle φ being in this case 0–5°. The appearance of a second substituent on the α-carbon atom leads to a diminution in the angle φ.

Electron spin resonance spectra of radicals have recently been obtained by the irradiation of frozen monomers such as isobutene[65], methyl methacrylate[36], and methacrylonitrile[33]. These spectra are attributed to $CH_2-\dot{C}(CH_3)X$ radicals, but the hyperfine structure constants for the β-protons differ from the values in Table 4. The discrepancy can be explained on the assumption that the angle φ in the radicals of the irradiated monomers is ~ 15° instead of 0–5°. The reasons for the appearance of such a conformation in the solid-phase polymerisation of monomers are still not clear.

With rise in temperature from 80° to 320°K the β-protons remain non-equivalent in the e.s.r. spectrum of $CH_2-\dot{C}(CH_3)X$ radicals[50]. The energy barrier to conformational transitions is lower in $CH_2-\dot{C}HX$ than in $CH_2-\dot{C}(CH_3)X$ radicals, and in the liquid phase at room temperature the β-protons become equivalent[24,27].

(*c*) $CXY-\dot{C}H-CXY$ and $CH_2-\dot{C}X-CH_2$ radicals

Table 5 gives the parameters of the e.s.r. spectra for "central" radicals of types (III) and (IV). In polymers containing quaternary carbon atoms in the main chain—poly(methyl methacrylate), polyisobutene, poly-α-methylstyrene—the spectrum of the $CXY-\dot{C}H-CXY$ radicals is a doublet with a separation of 21 oersteds. In polyformaldehyde ($O-\dot{C}H-O$ radicals) the splitting on the α-proton is considerably smaller: $a_H(\alpha) = 15$ oersteds. In polymers containing tertiary carbon atoms the hyperfine structure of the e.s.r. spectra of the $CH_2-\dot{C}X-CH_2$ radicals depends on the conformation of the radical.

The spectrum of the $CH_2-\dot{C}H-CH_2$ radicals in polyethylene comprises six hyperfine components, its overall width being 160–165 oersteds. With $a_H(\alpha) = 24.4 \times 0.84$ [? × 0.92 (Ed. of Translation)] = 22 oersteds the total splitting on the β-protons of each methylene group is $\frac{1}{2}(162 - 22) = 70$ oersteds. In order to obtain a six-component spectrum it must be supposed that the β-protons are already equivalent at 77°K: $a_H(\beta\text{-}1) = a_H(\beta\text{-}2) = 35$ oersteds. Barriers to internal movements are probably low in the polyethylene radical $-CH_2-\dot{C}H-CH_2-$.

The conformation of the chains in polymers of regular structure in the crystalline state has been established by means of X-ray and electron diffraction[74]. The conformation of a macromolecule, like that of a radical, can conveniently be characterised by the angles ψ of internal rotation about a C–C bond of the carbon skeleton. For the fragment $R_1-C_\beta H_2-C_\alpha HX-R_2$, for example, this is the angle between the projections of the $C-R_1$ and $C-R_2$ bonds on a plane perpendicular to the $C_\alpha-C_\beta$ bond.

For crystalline polymers having planar *trans*-bonds—polyethylene, poly(ethylene oxide), poly(vinyl alcohol)—the angle $\psi = 180°$. In polymers which crystallise in the form of 3_1-spirals (isotactic polypropylene and polybut-1-ene) the methylene groups on the left and on the right of the α-carbon atom ($CH_2-C_\alpha HX-CH_2$) are characterised by the angles $\psi_1 = 180°$ and $\psi_2 = 60°$.

The angle ψ may change on formation of a radical having its free valency in the middle of the polymer chain $CH_2-\dot{C}X-CH_2$. In all the polymer radicals investigated (Table 5) the two methylene groups are characterised by the same conformational angle (radicals have been observed in amorphous specimens of isotactic polypropylene and polybut-1-ene).

Table 6 gives the angles of internal rotation in polymeric molecules ψ and radicals ψ', together with the difference between them. The rotation of the portions of macromolecules about a C–C bond on abstraction of a hydrogen atom and formation of a radical is extremely large, amounting to several tens of degrees.

3. Conformations of Polymer Radicals

For all polymer radicals the hyperfine interaction constants of the α-protons vary within the range 15–22 oersteds depending on the nature and the number of substituents. The radical cannot contain more than two α-protons, and there is usually no difficulty about assigning their lines in the e.s.r. spectrum. The character of the spectrum—its width, number of components, intensity ratio—is determined in considerable measure by interaction of the unpaired electron with the β-protons, the number of which may reach 6–9. The splitting on each β-proton may vary from 0 to 50 oersteds, and is directly connected with the conformation of the radical, the angle of rotation about the $C(\alpha)-C(\beta)$ bond. When the conformational angles for the groups $C(\beta)H_2$ and $C(\beta)HX$ are known, the whole spectrum can be constructed for a given radical.

Theoretical calculation of the conformations of free radicals, like that of molecules, requires the many-elec-

Table 5. Parameters of e.s.r. spectra of "central" radicals at 80°K.

Structure of radical	Form of spectrum: No. of hyperfine components	Form of spectrum: Σa_H, oersteds	ρ	Q_α, oersteds	$a_H(\alpha)$, oersteds	$a_H(CH_3)$, oersteds	$a_H(\beta\text{-}1)$, oersteds	$a_H(\beta\text{-}2)$, oersteds	φ^*	Production of radical	Ref.
$-CH_2-\dot{C}H-CH_2-$* Polyethylene	6	162	0.85	25	21	—	35	35	70	M,R,UV	1, 2, 11, 66
$-CH_2-\dot{C}(CH_3)-CH_2-$ Polypropylene**	6	130	0.78	—	—	23	30	3	25	M	19
$-CH_2-\dot{C}(C_2H_5)-CH_2-$ Polybut-1-ene	4	88	0.78	—	—	—	29	2	20	M,R	67, 68
$-CH_2-\dot{C}(OH)-CH_2-$ Poly(vinyl alcohol)	3	70	0.71	—	—	—	35	1	37	R	7
$-O-\dot{C}H-CH_2-O-$ Poly(ethylene oxide)	3	36	0.77	18	15	—	21	3	13	M	21
$-CO-NH-\dot{C}H-CH_2-$ Polycaprolactam	5	75	0.70		18	—	37	19	68	M,R	4, 17, 69
$-O-\dot{C}H-O-$ Polyformaldehyde	2	15	0.70		15	—	—	—	—	M,R	5, 21
$-C(CH_2)(COOCH_3)-\dot{C}H-$ $-C(CH_3)(COOCH_3)-$ Poly(methyl methacrylate)	2	21	0.85	25	21	—	—	—	—	M	13, 70
$-C(CH_3)_2-\dot{C}H-C(CH_3)_2-$ Polyisobutene	2	21	0.85	25	21	—	—	—	—	M,R	5, 6, 70
$-C(CH_3)(C_6H)_5-\dot{C}H-$ $-C(CH_3)(C_6H_5)-$ Poly-α-methylstyrene	2	21	0.85	25	21	—	—	—	—	M	70

*For radicals containing two or three β-methylene groups they all have the same conformation. For the radical $CH\beta_1H\beta_2-\dot{C}X-CH\beta_3H\beta_4$, for example, $a_H(\beta_1) = a_H(\beta_3)$ and $a_H(\beta_2) = a_H(\beta_4)$.
**The structure of the radicals formed by the irradiation of polypropylene has not yet been established unambigously, in spite of the large amount of work done [71-73].

tron problem to be solved, and has not yet been accomplished. However, analysis of the experimental data enables several qualitative relations to be established for the effect of various substituents on the conformation of alkyl radicals and on the height of the potential barrier determining the frequency of conformational transitions.

The angle of rotation about the $C_{(\alpha)}-C_{(\beta)}$ bond is determined by interaction of the substituents on the α-, β-, and γ-carbon atoms both among themselves and with neighbouring molecules. At low temperatures the e.s.r. spectra of a given radical in different matrices are usually the same: i.e. the medium in which the radicals are distributed probably has no effect on their conformation, and intermolecular interactions can be disregarded to a first approximation‡.

In all alkyl radicals having a β-methyl group $H_3C-\dot{C}XY$ the barrier to rotation about the $H_3C-C_{(\alpha)}$ bond is low, not exceeding 100 cal mole^{-1}; the methyl groups rotate freely down to 10°K. [59,75] On passing to radicals containing a β-methylene group $R-CH_2-\dot{C}XY$ (and also $>CH-\dot{C}XY$) the height of the barrier to internal rotation about the $C_\alpha-C_\beta$ bond rises sharply (by factors of 10–100); the equilibrium conformation of the radical is governed by the energetically most favourable relative arrangement of the substituents attached to the α- and β-carbon atoms. The sharp rise in the barrier is connected with the change in symmetry of the substituent (from C_{3V} for the CH_3 group to C_{1V} for RCH_2) when one of the methyl hydrogen atoms is replaced by an alkyl group R. The rise in the barrier can be regarded as resulting from interaction of the group R with the α-substituents X, Y and the unpaired electron.

‡ The height of the potential barrier to internal movements in the radicals, i.e. the temperature dependence of the hyperfine structural constants, is probably connected with the nature of the matrix.

Table 6. Change in conformation of polymer chain on formation of "central" radicals.

Polymer	Radical	ψ^* (mol.)	ψ' (radical)	$(\psi - \psi)^\circ$
Polyethylene	$R-CH_2-\dot{C}H-CH_2-R$	180	160	20
Poly(vinyl alcohol)	$R-CH_2-\dot{C}(OH)-CH_2-R$	180	127**	53
			53	127
Poly(ethylene oxide)	$R-O-\dot{C}H-CH_2-O-R$	180	103	77
			77	103
Polypropylene	$R-CH_2-\dot{C}(CH_3)-CH_2-R$	180	115	65
		60	115	55
			65	5
Polybut-1-ene	$R-CH_2-\dot{C}(C_2H_5)-CH_2-R$	180	110	70
		60	110	50
			70	10

*From Ref. 74.
**The ambiguity in the value of the angle ψ' for the radical is due to the two possible orientations of the group R relative to the orbital axis of the unpaired electron.

In the simplest terminal radical $CH_2-CH_2-\dot{C}H_2$ (polyethylene, Table 3) let us denote by R the polymer chain beginning with the γ-carbon atom. The conformation of the radical is shown in Fig. 5*a*. The angle of rotation about the $C_{(\alpha)}-C_{(\beta)}$ bond is determined to a first approximation by the interaction of the group R with the α-substituents—the two hydrogen atoms and the unpaired electron—and has the value 68°. The group R is remote from the orbital of the unpaired electron (the *Z*-axis): i.e. it is more strongly repelled from it than from the hydrogen atoms.

In the radical $CH_2-\dot{C}(CH_3)_2$ (polyisobutene, Fig. 5*b*, $\varphi = 2°$) the substituent R is "overshadowed" by the orbital of the unpaired electron. Consequently the most important factor here is repulsion of the group R from the α-methyl groups, while interaction with the unpaired electron is less effective.

It is seen from these two examples that, in alkyl radicals, repulsion of the β-group R (CH_3, C_2H_5, etc.) from the α-substituents becomes stronger in the sequence

$$\text{Hydrogen atom} < \text{Unpaired electron} < \text{Alkyl substituent} . \qquad (12)$$

This sequence is consistent also with an analysis of a large number of e.s.r. spectra for the lower alkyl radicals, and can be used to predict the conformations of alkyl radicals having various structures.

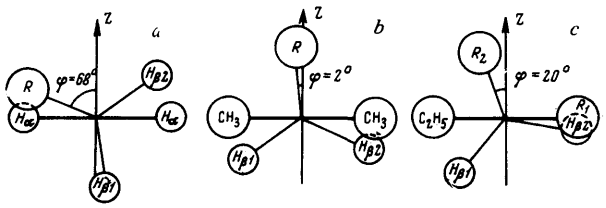


Figure 5. Conformation of polymer radicals:
a) terminal radical in polyethylene $R-CH_2-\dot{C}H_2$;
b) terminal radical in polyisobutene $R-CH_2-\dot{C}(CH_3)_2$;
c) central radical in polybut-1-ene $R_1-\dot{C}(C_2H_5)CH_2-R_2$.

The conformations of the radicals in polyalkenes (Tables 3–5) show good consistency with the requirements of the sequence (12). As example let us examine the conformation and the e.s.r. spectrum of radicals having the free valency in the centre of the chain in polybutene

$$R_1\underset{(3)}{-CH_2-}\underset{(1)}{\dot{C}}(C_2H_5)\underset{(2)}{-CH_2-}R_2$$

(Fig. 5*c*). There is no generally accepted interpretation of the e.s.r. spectrum of this radical[67,68]. We shall regard the 1-ethyl group and the right-hand part of the chain as substituents on the α-carbon atom. The group R_1 (the left-hand portion of the polymer chain) is repelled from the alkyl substituents CH_2-R_2 and C_2H_5 more strongly than from the unpaired electron; consequently the angle should be small, and from the graph in Fig. 2 the splitting on one β-proton will be negligible, while that on the other will be close to half the maximum value ($Q_{\beta\rho}$). The conclusion remains unchanged if the groups C_2H_5, R_1, and R_2 change places: i.e. only one β-proton will be involved in the splitting in each of the three methylene groups, and the e.s.r. spectrum should be a quadruplet 70–80 oersteds wide. The spectrum observed on the radiolysis and the mechanical degradation of amorphous polybutene actually comprises four hyperfine lines with $a_H(\beta) = 29$ oersteds.

Prediction of the conformations (and the e.s.r. spectra) of radicals containing the substituents CN, NH_2, COOH, $OCOCH_3$, C_6H_5, etc. is difficult because of differences in the nature of the forces of interaction between polar groups, groups capable of forming hydrogen bonds, etc. For radicals $CH_2-\dot{C}XY$, where X and Y are bulky substituents, the conformation can be established by constructing models.

Fig. 6 shows as example photographs of models of the terminal radicals in (*a*) polyethylene and (*b*) polyisobutene. The photographs illustrate the role of steric hindrance in determining the conformation of the radicals. In polyethylene the hydrogen atoms are freely arranged, and rotation to any angle is in principle possible about the $C(\alpha)-C(\beta)$ bond. In polyisobutene the chain is considerably more compact, and the angle of rotation about the $C(\alpha)-C(\beta)$ bond in the terminal radical is restricted to values at which the van der Waals radii of the substituents do not overlap. In poly(methyl methacrylate) and poly-α-methylstyrene the possible conformation of terminal radicals found from electron models agrees with results obtained by the e.s.r. method (Table 5).

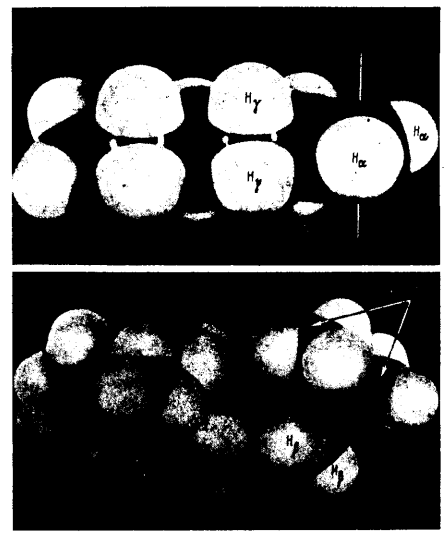


Figure 6. Models of the radicals $\sim CH_2-CH_2-\dot{C}H_2$ (polyethylene) and $\sim CH_2-C(CH_3)_2-CH_2-\dot{C}(CH_3)_2$ (polyisobutene). The axis of the orbital of the unpaired electron is shown by the white line.

Thus the conformations of alkyl radicals and certain complicated substituted radicals can be predicted from a consideration of the forces of interaction between the substituents and an examination of electron models. The accuracy with which the conformational angles can be predicted is not good (10–15°), but even such estimates are of great value in analysing poorly resolved e.s.r. spectra of polymer radicals in the solid phase.

III. CHEMICAL PROPERTIES AND STABILITY OF POLYMERIC RADICALS

The chemical behaviour of polymer radicals at low temperatures is governed primarily by the reactivity of the radicals and the molecules with which they interact, and secondarily by the possibility of encounters and contacts between the reactant species. These two factors are undoubtedly closely interlinked.

The lifetime of radicals in solid polymers may be unlimited, the reason being solely the impossibility of their moving and meeting one another. Under the most favourable conditions (rubbers of low molecular weight in a highly elastic state) the coefficient of self-diffusion at 370°K does not exceed 10^{-13}–10^{-14} $cm^2\ s^{-1}$:[76,77] i.e. several hours are required to overcome a distance of 10^2–10^3 Å [$x = (2Dt)^{\frac{1}{2}}$], where D is the coefficient of self-diffusion, x the diffusion

distance, and t the time]. In the vitreous state the movement of macromolecules is retarded, and radicals in such systems are said to be frozen.

The rate of diffusion of substances of low molecular weight in solid polymers is also low, usually less than the rate of many chemical reactions. Thus the rate of interaction with monomers of chain carriers is governed by the diffusion of these compounds to the polymer radicals [78]. The addition of oxygen molecules to polymeric alkyl radicals in films and massive specimens is also limited by the diffusion of oxygen [78,79].

In analysing the kinetics of reactions in highly viscous media use is made of the concept of a cage, cell, or element of volume, inside which the particles react with one another. In order to react, the particles must be present in the same cage. An important factor in decomposition reactions is the escape of the newly formed particles from the cage. This approach was first formulated by Frank and Rabinowitch [80], and is now generally accepted. The e.s.r. method has recently been used to detect polymer radicals [81] and those of low molecular weight [82] at distances of several Ångström units from one another.

The formal kinetic equation for the rate of a bimolecular reaction in the solid phase, which takes into account the stages of migration of active centres when their distribution is homogeneous§ and interaction of the reactant particles in a single element of volume, is [84]

$$\frac{dC_A}{dt} = k_m C_A \ln\left(1 - \frac{k_i V^* C_B}{k_i + k_m}\right) \qquad (13)$$

where C_A and C_B are the concentrations of the mobile reactant A particles and the stationary reactant B particles, k_m is the frequency (in s^{-1}) with which A particles jump from one cage to another, k_i (s^{-1}) the reaction rate constant inside the cage, and V^* the volume of the cage.

When $k_i V^* C_B \ll k_i + k_m$ the kinetic law is described by the usual second-order equation

$$-\frac{d\bar{C}_A}{dt} = k_{eff} C_A C_B \qquad (14)$$

where

$$k_{eff} = \frac{k_i \cdot k_m}{k_i + k_m} \cdot V^*. \qquad (15)$$

When radicals combine with one another in solid polymers, the rate of migration is always less than the reaction velocity in the cage ($k_m \ll k_i$), so that

$$\frac{dc}{dt} = 2k_m C \ln(1 - V^* C) \ . \qquad (16)$$

In most cases the rate constant and the activation energies for the reactions of radicals in solid polymers are characteristic of the process of migration of the free valency (k_m)¶, not the actual chemical activity of the reactant species (k_i). This category of experimental data includes the results of numerous kinetic investigations of the destruction of radicals in polymers [85-90], as well as individual measurements of the rate constants for reactions of radicals with monomers and chain-transfer agents [78].

Information on the reactivity of radicals has been obtained in systems in which polymer radicals are surrounded by reactant molecules. This case is realised firstly in the interaction of radicals with neighbouring molecules of their own polymer, and secondly in the reactions of polymer radicals distributed in a matrix of a chemically reactive substance of low molecular weight. The method of studying the reactivity of polymer radicals in frozen dilute solutions is based on this principle [23,91,92]. The polymer radicals are generated by mechanical treatment of the solution.

Mechanical grinding of frozen dilute solutions results in cleavage of the macromolecules at bonds in the main chain, with the formation of terminal polymer radicals $\cdot R_0$, which then react with the surrounding solvent molecules. In the course of grinding, fine particles are deformed, and individual layers of material are displaced relative to one another; under such conditions the reaction velocity is proportional to the reactant concentrations:

$$\frac{d[R_0^{\cdot}]}{d\tau} = W - k_i [R_0^{\cdot}] [M] \qquad (17)$$

and

$$\alpha = \frac{1}{k_i [M] \tau} (1 - e^{-k_i [M] \tau});$$

when

$$\tau \gg k_i [M] \quad \alpha \simeq \frac{1}{k_i [M] \tau} \qquad (18)$$

where W is the rate of formation of initial $\cdot R_0$ polymer radicals, while τ is the duration of dispersion, k_i is the rate constant for reaction of these radicals with surrounding molecules of the reactant M, and $\alpha = [\cdot R_0]/([\cdot R_0] + [R\cdot])$, with $[R\cdot]$ the concentration of radical reaction products and $1 - \alpha$ the degree of conversion.

The accuracy with which α can be determined from e.s.r. spectra is usually low, and only the order of magnitude of the rate constant can be estimated by this method.

The literature contains hardly any rigorous or systematic data on the temperature dependence of the rates of the elementary reactions undergone by polymer radicals in the solid phase, so that approximate procedures must be used to estimate activation energies. When the polymer radical and the reactant molecule are located in the same cage, in a state of continuous contact as it were, the reaction velocity will be a maximum, and the pre-exponential factor in the Arrhenius equation cannot exceed 10^{13} s^{-1}. Under ordinary conditions transformations of radicals can be detected if their concentration changes appreciably during the course of hours or tens of hours, i.e. if $k \simeq 10^{-4}$–10^{-5} s^{-1}. Hence

$$E \leqslant 2.3RT \lg \frac{k_0}{k} \quad \text{or} \quad E \leqslant 80T. \qquad (19)$$

Thus if the temperature at which a particular elementary reaction takes place is known, an upper limit to possible values of the activation energy can be estimated. For example, it follows from the relation (19) that reactions having an activation energy exceeding 6 kcal $mole^{-1}$ will not be observed at the boiling point of nitrogen (80°K).

Reactions involving addition, substitution, decomposition, and combination are characteristic of free radicals. All these classes of elementary reactions play an important part in the chemistry and the physical chemistry of polymers; they take place under the influence of ionising radiations, ultraviolet irradiation, mechanical constraints, aging and fatigue, chemical modification, thermal and thermo-oxidative degradation of polymeric materials, etc. Published data on elementary reactions in the solid phase are fragmentary, authors most often confining themselves

§ The kinetic laws of reactions in non-homogeneous non-uniform systems are considerably more complicated. An example of such a reaction is the "stepwise" recombination of radicals in irradiated solids, which has been analysed in Ref. 83.

¶ The form of the constant k_m is discussed in Ref. 78.

to reporting the fact of interaction and analysing the reaction products; more rarely rate constants are measured, and only in isolated cases are the activation energy and the pre-exponential factor determined. The results of investigations of the reactivity at low temperatures of polymer radicals in the principal classes of reactions are examined below. The elementary reactions of addition, substitution, and decomposition are analysed separately from those involving the destruction of radicals, the rates of which in solid polymers are always determined by processes of migration of the free valency.

1. Elementary Addition, Substitution, and Decomposition Reactions

Addition reactions

Addition reactions include the interaction of polymer radicals with substances containing double or triple bonds (including aromatic compounds), oxygen, nitric oxide, and other unsaturated molecules. The reactions between radicals and vinyl monomers have been studied in the greatest detail [22,78]†.

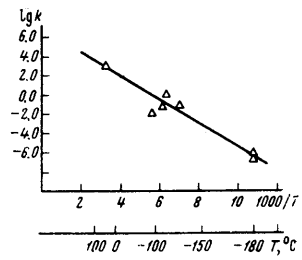


Figure 7. Temperature dependence of rate constant for the addition of certain monomers (styrene, α-methylstyrene, methyl acrylate, and acrylic acid) to $\sim CH_2-\dot{C}(CH_3)(COOCH_3)$ radicals.

Rate constants for addition of the monomers have been measured at low temperatures (80–100°K) in frozen solutions [22]. The dependence of the addition rate constant for radicals of poly(methyl methacrylate) on temperature over the range 100–400°K is shown in Fig. 7 plotted as $\lg k$ against $1000/T$. The upper left-hand point corresponds to the rate constant of chain growth in the liquid-phase polymerisation of methyl methacrylate; over the range 330–380°K we have $k = 6 \times 10^5 \exp(-4700/RT)$ M^{-1} s^{-1}, [93] and the slope of the straight line has been determined from these data. The points in the lower right-hand part of the graph correspond to measurements of the rate constant for the addition of various monomers (styrene, α-methylstyrene, methyl acrylate‡) to radicals of poly(methyl methacrylate) $CH_2-\dot{C}(CH_3)(COOCH_3)$ in frozen solutions [22]. The values of $k_{100°K}$ for various monomers lie in the range 10^{-5}–10^{-4} M^{-1} s^{-1}. The graph shows that to a first approximation the activation energy and the pre-exponential factor remain the same in the solid phase at low temperatures as in the liquid phase at 350–400°K.

Fused-ring aromatic compounds (anthracene, acridine) and quinones (benzoquinone, tetrachlorobenzoquinone) readily add to the terminal radicals of poly(methyl methacrylate), polystyrene, and other vinyl polymers at 100°K. [92] The addition rate constants for these compounds at 100°K vary over the range 10^{-6}–10^{-4} M^{-1} s^{-1}.

The polymer radicals $-CHX-\dot{C}H_2$, $-CH_2-\dot{C}H(OCOCH_3)$, and $-CH_2-\dot{C}H(COOCH_3)$ are the most active in addition reactions at low temperatures. They are approached by $-CH_2-\dot{C}H(C_6H_5)$ radicals. The last position in the sequence is occupied by $-CH_2-\dot{C}(CH_3)(COOCH_3)$ and $-CH_2-\dot{C}(CH_3)(C_6H_5)$ radicals. The addition of monomers to central radicals of the type $-CXY-\dot{C}H-CXY$ has not been observed in frozen solutions. The same sequence of activities is maintained in reactions with quinones, anthracene, and acridine [92].

In the solid phase at low temperatures $-CH_2-\dot{C}H(C_6H_5)$ radicals are more active than $-CH_2-\dot{C}(CH_3)(COOCH_3)$ radicals; this is inconsistent with the theory of ideal reactivity and results for the liquid-phase copolymerisation of monomers [93]. It may be assumed that the steric factor plays a more important part in the solid than in the liquid phase. Therefore radicals having the structure $-CH_2-\dot{C}HX$ are generally more active than $-CH_2-\dot{C}(CH_3)X$ radicals, while radicals having the free valency in the middle of the chains, of the type $-C(CH_3)X-\dot{C}H-C(CH_3)X-$, such as poly(methyl methacrylate), etc., do not undergo addition reactions at all in frozen solutions.

Oxygen reacts with all alkylated polymeric radicals at temperatures of 150–200°K and below [11,78,79,90,94,95], with the formation of peroxy-radicals ROO•, distinguished by a characteristic anisotropic e.s.r. signal [5]. Peroxy-radicals have been observed in polyethylene [8], polypropylene [5,96], poly(vinyl chloride) [89,94], polystyrene [78], poly(methyl methacrylate) [78,85,95], and other carbon-chain and heterochain polymers, including those which occur naturally. The addition of oxygen has been studied in massive specimens [79], films [96], turnings [78], and finely divided powders [95]. When the material is sufficiently thick, oxidation is limited by the diffusion of oxygen inside the polymer [78,79].

The activation energy of the reaction $R\cdot + O_2 \rightarrow ROO\cdot$ has the values 6, 5.3, 5.9, and 7.9 kcal $mole^{-1}$ for polytetrafluoroethylene [79], polystyrene [78], poly(vinyl acetate) [78], and poly(methyl methacrylate) [78].

A summary of kinetic results for the reactions of polymer radicals with various molecules (O_2, NO, etc.) from the gas phase will be found in Ref. 90.

Substitution reactions

The chief reactions studied have been those involving abstraction of a hydrogen atom by a polymer radical from neighbouring macromolecules [19,20,97] or compounds of low molecular weight having weak C–H, N–H, O–H, or S–H bonds [92]. Intermolecular transfer of a hydrogen atom probably plays an important part in the stabilisation of radical states in solid polymers.

Polymer radicals of the type $R-CXY-\dot{C}H_2$ exhibit the highest activity [92] in $R\cdot + HR_1 \rightarrow RH + R_1\cdot$ reactions. In frozen dilute solutions, with HR_1 representing an aromatic hydrocarbon (toluene, ethylbenzene, isopropylbenzene, etc.), reaction at 80–100°K yields the simple radicals

† Solid-phase polymerisation is not discussed in the Review.

‡ It is impossible by the e.s.r. method to observe the interaction of poly(methyl methacrylate) radicals with methyl methacrylate.

$C_6H_5\dot{C}H_2$, $C_6H_5\dot{C}HCH_3$, $C_6H_5\dot{C}(CH_3)_2$, etc., which have all been recorded by the e.s.r. method [64]. On passing from toluene to ethylbenzene the reaction rate constant increases several times to reach 10^{-5} M^{-1} s^{-1}, in conformity with the decrease in strength of the C–H bond. It follows from the relation (19) that the activation energy for abstraction of a hydrogen atom from toluene cannot exceed 7–8 kcal mole^{-1}. For the reaction of methyl radicals with toluene vapour at 400–600°K we have $k = 10^8 \exp(-8300/RT)$ M^{-1} s^{-1}: [98] i.e. the activation energy for transfer of a hydrogen atom to R–CXY–$\dot{C}H_2$ radicals in the solid phase is lower than—or in the extreme case equal to—the activation energy of the analogous reaction for simple methyl radicals in the gas phase.

The reaction of terminal radicals of polyethylene with a neighbouring chain

$$-CH_2-\dot{C}H_2+-CH_2-CH_2-CH_2- \longrightarrow -CH_2-CH_3+-CH_2-\dot{C}H-CH_2-$$

which occurs at a measurable rate at 140°K, has an activation energy of only 4 ± 1 kcal mole^{-1}. [19] Yet for the reaction of methyl radicals with butane in the gas phase E = 8.3 kcal mole^{-1}. [98] Thus the transfer of a hydrogen atom to R–$\dot{C}H_2$ radicals, whether in polyethylene or in frozen solutions of aromatic hydrocarbons (toluene, ethylbenzene, etc.), is possible at low temperatures (110–140°K), and has an unexpectedly low activation energy§.

The radicals R–CH_2–$\dot{C}HX$ and R–CH_2–$\dot{C}XY$ are less active than are R–$\dot{C}H_2$ radicals, and do not interact with hydrocarbons at low temperatures [92]. There is almost no information on the reactions of these radicals with "their own" macromolecules. Only in polypropylene at 140°K are terminal radicals CH_2–$\dot{C}H(CH_3)$ converted into central radicals [19]. In poly(methyl methacrylate), polystyrene, and several other polymers the terminal radicals are stable up to 330–350°K and above (see Tables 9 and 10), which is evidence of their low activity in reactions involving the transfer of a hydrogen atom.

Peroxy-radicals ROO• react with various types of polymer molecules—polycaprolactam, polystyrene, poly(methyl methacrylate), etc.—and in a vacuum at 200–270°K we can observe the conversion of ROO• into R• radicals, accompanied by a usually appreciable fall in the total concentration of radicals [97]. The primary act is transfer of a hydrogen atom to the peroxy-radical with formation of a polymer radical having the free valency in the middle of the chain. The rate constant of this reaction has been measured by two different methods (chemiluminescence and e.s.r.) in poly(methyl methacrylate) [97]. Over the temperature range 250–360°K,

$$k = 10^{6\pm1} \exp\left(-\frac{12000 \pm 2000}{RT}\right) \ M^{-1}\ s^{-1}$$

the product of the reaction being –$C(CH_3)(COOCH_3)$–$\dot{C}H$–$C(CH_3)(COOCH_3)$– radicals. In polypropylene [100] $k = 10^{5.3} \times \exp(-9000/RT)$ (at 380–410°K). There are no published data on the rate of this reaction for other polymers, but since the conversion ROO• → R• is observed over roughly the same temperature range, the activation energy will not greatly change on passing to other polymers.

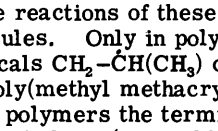
Table 7 gives rate constants for reactions of the radicals R–$\dot{C}H_2$, R–CH_2–$\dot{C}HX$, R–CH_2–$\dot{C}XY$, and ROO• with a series of compounds containing a reactive hydrogen atom (aromatic amines, phenols, thiols, etc.) [92]. The rate constants were measured in frozen dilute solutions, where the polymer radicals were surrounded by molecules of the reactant (see relation 18).

Polymer radicals of varying structure differ from one another in reactivity considerably more strongly in substitution than in addition reactions. Radicals for which data are available on their chemical activity in hydrogen-transfer reactions from phenols, amines, and thiols can be arranged in the sequence [92]

$$\left\{\begin{array}{l} R-\dot{C}H_2 \\ -CH_2-\dot{C}H(OCOCH_3) \\ ROO^{\bullet} \end{array}\right\} > -CH_2-\dot{C}H(C_6H_5) > -CH_2-\dot{C}(CH_3)X$$

where X = CH_3, C_6H_5, $COOCH_3$. For R–$\dot{C}H_2$, –CH_2–$\dot{C}H(OCOCH_3)$, and ROO• radicals the transfer rate constants at 100°K always exceed 10^{-4} M^{-1} s^{-1}. The activity of the peroxy-radicals is almost independent of the structure of the carbon skeleton. The rate constant for the interaction of –CH_2–$\dot{C}(CH_3)(COOCH_3)$ radicals with phenols and amines at 100°K is less than 10^{-7} M^{-1} s^{-1}.

Table 7. Rate constants of elementary substitution reactions for alkyl (R•) and peroxide (ROO•) polymer radicals with certain compounds at 80–100°K.

Reactant	Initial radical	k, M^{-1} s^{-1}
$C_6H_5CH_3$, $C_6H_5CH_2CH_3$	R•*	10^{-6}–10^{-5}
	R•	$\sim 10^{-5}$
	ROO•	$\geqslant 10^{-4}$
C_6H_5–NH–C_6H_5	R•	10^{-6}–10^{-4}
	ROO•	$\geqslant 10^{-4}$
C_6H_5–SH	R•	—
	ROO•	$\geqslant 10^{-4}$
$(C_6H_5)_3$ C–Cl	R•	10^{-6}–10^{-5}

*R• = –CHX–$\dot{C}H_2$, –CH_2–$\dot{C}HX$, –CH_2–$\dot{C}XY$.

Decomposition reactions

The decomposition of polymer radicals plays an important part at high temperatures in processes of thermal and thermo-oxidative degradation [101,102]. Recently the decomposition of polymer radicals has been detected even at room temperature [97].

The simplest decomposition reaction is depolymerisation—detachment of a monomer from a terminal polymer radical:

$$-CH_2-CXY-CH_2-\dot{C}XY \rightarrow -CH_2-\dot{C}XY + CH_2{=}CXY$$

Elimination of a monomer is the opposite reaction to polymerisation, and its activation energy is $E_d = E_{gr} + Q$, where E_{gr} is the activation energy of chain growth during polymerisation and Q is the heat of polymerisation. Values of E_d, E_{gr}, and Q for various polymers are listed in Table 8. The activation energy of depolymerisation is largest in polyethylene, where it reaches 28 kcal mole^{-1}. Methyl methacrylate is characterised by low values of Q and E_{gr}, and depolymerisation is the principal way in which poly(methyl methacrylate) decomposes [101]. The rate of depolymerisation of poly(methyl methacrylate) to be expected at room temperature is

$$W = k_0 \exp\left(-\frac{18000}{1.98 \cdot 290}\right)[R^{\bullet}] = 10^{-8}[R^{\bullet}]$$

§ Methyl radicals also have enhanced activity in the solid phase: at 77°K they abstract a hydrogen atom from a polyphenylmethylsiloxane molecule [99].

The rate of separation of monomer is a specimen of the polymer containing 10^{17}-CH_2-$\dot{C}(CH_3)(COOCH_3)$ radicals was close to the calculated value[86].

Modes of decomposition of polymer radicals other than depolymerisation are also possible. Mainly alkylated derivatives of benzene—toluene, ethylbenzene, isopropylbenzene—separate in polystyrene[97]. These compounds are probably formed by the breakdown of central radicals with further separation of radicals of low molecular weight by reactions of the type

$$\sim R^{\cdot}\sim \rightarrow \sim \Pi + R^{\cdot}\sim$$
$$\sim R^{\cdot} \rightarrow \sim \Pi + r^{\cdot}$$

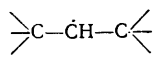
where Π represents the polymer and r• the simple radical.

Table 8. Some parameters of processes of polymerisation[93] and depolymerisation.

Monomer	Q, kcal mole^{-1}	E_{gr}, kcal mole^{-1}	E_d, kcal mole^{-1}
Ethylene	22.3	5.5[103]	27.8
Vinyl acetate	21.3	4.2	25.5
Styrene	16,1—16,7	7.2	23—24
Methyl acrylate	18.7	4.7	23.4
Methyl methacrylate	13.0	4.7	17.7

"Volatile" radicals r• have been detected by the e.s.r. method among the products of the radical degradation of polyethylene and polypropylene at high temperatures[102]. Whether breakdown of the central radical ~R•~ and ejection of the simple radical r• take place in a single act or in two stages in unknown.

No study has been made of the kinetics of the breakdown of radicals having the free valency in the middle of the chain. In poly(methyl methacrylate) the



radicals decompose at lower temperatures than do $-CH_2-\dot{C}(CH_3)(COOCH_3)$ radicals[86]. Radicals having their free valency in the middle of the chain probably break down more easily than do terminal radicals in other polymers, too. However there is as yet no direct evidence to support this suggestion.

2. Nature of Processes of Migration of the Free Valency and the Destruction of Radicals

The loss of radicals in solid polymers is the most convenient reaction for investigating the nature of the processes involving migration of the free valency. Decay of polymer radicals may be due either to diffusion or to chemical mechanisms of transfer of the free valency. Analysis of the conditions for destruction will give the first information on the nature of processes involving migration of the free valency in polymers of various structures. Data on the stability of alkylated and peroxide radicals of various types in vinyl polymers and in polyoxides are assembled in Table 9¶. The measure of stability adopted in compiling Table 9 was the temperature range within which the concentration of radicals of the given type drops sharply when the specimens are heated. In some polymers, radicals of one type disappear by being converted into other, more stable radicals; in this case the total radical concentration either diminishes or remains constant.

Table 9. Temperature range of destruction of polymer radicals.

Polymer	T_{ds}, °K Refs.104, and 105	Temperature of stability, °K			
		R—$\dot{C}H_2$	R—$\dot{C}XY$	"central radicals"	ROO•
Polyethylene	188	120—140[19, 20]	—	260—280[106, 107]	260—280[106, 108]
Polypropylene	256	<90	120—140[19]	250—290[19]	300[108]
					300—340[96]
Polyisobutene	200	<90	200—220	200—220	200—220
Polystyrene	370	120—140*	330—350[111]	—	260—280[111]
Poly(methyl methacrylate)	380—390	<90*	330—350[85, 86, 111]	250—270[86]	260—280[86, 97]
Poly(vinyl alcohol)	358	120—140[21]*	—	330—360[109]	200—220
Polyformaldehyde	250	250—270[80]		350—370[80, 87]	200—220
Polycaprolactam	320	120[20]	—	280—290[17]	

*Data for frozen solutions of polymers in inert solvents.

In a rigorous approach the stability must be characterised by the rate constant of destruction or by the constants k_0 and E in the Arrhenius expressions. Such measurements are collected together in Table 10. They relate to cases in which the loss of radicals obeys a second-order equation. With the values of k_0 and E known, we can estimate the temperature limits of stability, i.e. the range within which the lifetime of the radicals decreases to minutes ($10^4 > \tau > 10^2$ s), while the destruction rate constants lie in the range $10 > k_{ds} > 10^{-1}$ M^{-1} s^{-1} {with destruction having second-order kinetics $k_{ds} \simeq 1/\tau[R^{\cdot}]$; usually $[R^{\cdot}] = 0.001$ M}. In several polymers radicals of different types (terminal, central, and peroxide) are destroyed under roughly the same conditions, at temperatures above the glass point of the polymer, in air and in a vacuum; in such a case diffusion may be expected to make a great contribution to migration of the free valency. The primary example of such polymers is polyisobutene (Table 9). In polystyrene, poly(methyl methacrylate), and other polymers radicals of different types differ markedly in their stability. It may be assumed that in these polymers the mechanism of migration of the free valency is determined not so much by the flexibility of the macromolecules as by the structure and the chemical activity of the radical.

Radicals of type R-$\dot{C}H_2$

The radicals are usually stable at temperatures below 150°K. Under these conditions at a diffusion mechanism of migration is excluded, and their disappearance is most likely due to their great activity in reactions involving the intramolecular and intermolecular transfer of a hydrogen atom. The example of polyethylene (subsection 1) shows that the term "destruction" is inexact in relation to R-$\dot{C}H_2$ radicals: they interact with a neighbouring polymer chain, and are converted into more stable radicals with the free

¶ The stability of radicals depends on the state of the polymer, but this aspect has not yet been investigated systematically. Radicals are more stable in crystalline than in amorphous specimens (polypropylene[110], polybutadiene[67]).

valency in the middle of the chain[19]. At low temperatures this process is limited. At higher temperatures (260–280°K) the loss reactions develop further, and the total concentration of radicals falls.

The activity of R–CHX–$\dot{C}H_2$ radicals depends little on the nature of the substituent X, and under otherwise similar conditions the reaction velocity is determined by the stability of the C–H bonds in the polymer molecule. The stability of these bonds is greatest in polyethylene, and therefore R–$\dot{C}H_2$ radicals are most easily detected in this polymer. The radicals R–O–$\dot{C}H_2$ are less active than R–CHX–$\dot{C}H_2$, and in polyformaldehyde transfer of a hydrogen atom begins to play a part at temperatures above 250°K.

Table 10. Rate constants of the destruction of alkyl and peroxide polymer radicals.

Polymer	Radicals	E, kcal mole^{-1}	$\lg k_0$ (M^{-1} s^{-1})	Refs.
Poly(vinyl acetate)		23	15	111*
Polystyrene	$-CH_2-\dot{C}H(C_6H_5)$	24	14	111*
Poly(methyl methacrylate)	$-CH_2-\dot{C}(CH_3)(COOCH_3)$	28	17	85
	$-CH_2-\dot{C}(CH_3)(COOCH_3)$	29	17	111*
	$-\overset{\vert}{C}-\dot{C}H-\overset{\vert}{C}-$	26	21	86
Poly(methyl acrylate)	$-CH_2-\dot{C}H(COOCH_3)$	44	31	31
Polyformaldehyde	$-O-\dot{C}H-O-$	19	14	87
Poly(vinyl chloride)		44	24	88
		38	20	89
Polypropylene		23	14	90
Poly(methyl methacrylate)	peroxide	17	12	86
	ditto	18	12	111**
Poly(vinyl acetate)	»	18	13	111**
Polystyrene	»	18	14	111**

*Values of k_0 given in Ref. 111 are probably wrong. The values of k_0 in Table 10 have been calculated by us from the data in Fig. 1 of Ref. 111.
**Values of E and k_0 calculated by us from data of Fig. 3 in Ref. 111.

Radicals of type R–CH_2–$\dot{C}XY$

The loss rate constants and activation energies for radicals of this type have been measured in poly(methyl methacrylate), polystyrene, poly(vinyl acetate), and certain other polymers (Table 10). These radicals differ markedly among themselves in stability. In polypropylene (see Table 9) transformations begin at 120–140°, but in poly(methyl methacrylate) and polystyrene the radicals are stable in a vacuum up to 350°K. Let us examine these extreme cases.

The CH_2–$\dot{C}H(CH_3)$ radicals in polypropylene probably disappear by the same mechanism as radicals of type R–$\dot{C}H_2$: The primary act is detachment of a hydrogen atom from a neighbouring chain. The former radicals should be more active than –CH_2–$\dot{C}H_2$ radicals in this reaction, but the C–H bonds are a few kilocalories less stable in polypropylene than in polyethylene. Therefore intermolecular transfer of the free valency is possible for both radicals at low temperatures.

In the activity sequence for substitution reactions CH_2–$\dot{C}(CH_3)(COOCH_3)$ radicals are nearly last (see subsection 1), and furthermore in the poly(methyl methacrylate) chain the methylene group containing the active hydrogen atom is located between quaternary carbon atoms carrying bulky substituents, so that migration of the free valency is sterically hindered. Nevertheless, breakdown (depolymerisation) of these radicals is quite rapid even at room temperature[86]. During depolymerisation the free valency moves along the chain at a speed of k_d chain units per second, and the possibility arises of encounters between radicals. If it is supposed that no energy barrier opposes the combination of radicals with each other, the loss rate constant with this mechanism of migration of the free valency is $k_m = k_d M/1000$ M^{-1} s^{-1}, where M is the molecular weight of the chain unit. At 330°K

$$k_d = 10^{12} \cdot \exp\left(-\frac{18000}{1.98 \cdot 330}\right) 10\ s^{-1}$$

whence $k_m \simeq 1$ M^{-1} s^{-1}, which coincides in order of magnitude† with the actual rate of loss at 330°K (Table 10), the conbination of each pair of radicals being accompanied by the separation of several monomer molecules[86]. At higher temperatures the rate of loss comes to exceed the calculated value ($E_{ds} = 28$ kcal, while $E_d = 18$ kcal). It is probable that, as the glass point is approached, migration of the free valency by a diffusion mechanism is not excluded.

Radicals with free valency in middle of chain

In poly(methyl methacrylate) these radicals become unstable at 250–270°K, and it may be supposed that the mobility of the free valency is largely due not to diffusion but to chemical reactions. At 250–300°K both hydrogen transfer and breakdown of the radicals may play a part. The relative rates of these reactions depend on the nature of the polymer:

$$\frac{W_{tr}}{W_d} = \frac{k_{o,tr}[M]}{k_{o,d}} \cdot \exp\left(\frac{E_d - E_{tr}}{RT_{st}}\right) \qquad (20)$$

where [M] is the concentration (molarity) of the polymer (in most cases $10 < [M] < 30$), $k_{o,tr}$ and E_{tr} are the preexponential factor and the activation energy for transfer of a hydrogen atom (it may be supposed that in solid polymers $k_{o,tr} \simeq 10^{6 \pm 1}$ M^{-1} s^{-1}—see subsection 1), and $k_{o,d}$ and E_d are the corresponding parameters for decomposition of the radicals (in order of magnitude $k_{o,d} \simeq 10^{12}$–10^{13} s^{-1}). Thus $W_{tr}/W_d = 10^{-5 \pm 1} \exp[(E_d - E_{tr})/RT_{st}]$. At $T_{st} = 250$–300°K with $E_d - E_{tr} > 8$ kcal mole^{-1}, we always have $W_{tr} > W_d$; conversely, when $E_d - E_{tr} < 6$ kcal mole^{-1}, the rate of decomposition will be higher than that of migration of the free valency.

In polyethylene and polypropylene $E_d > 25$ kcal mole^{-1}, while $E_{tr} < 15$ kcal mole^{-1}, i.e. $E_d - E_{tr} > 10$ kcal mole^{-1}, and near the stability temperature the rate of migration of the free valency should be much greater than the rate of decomposition of the radicals.

In polymers containing quaternary carbon atoms in the main chain E_d does not exceed 15–20 kcal mole^{-1} (Table 8) and $E_d - E_{tr}$ is small. In poly(methyl methacrylate)

† Under real conditions the probability of the reverse reaction increases as the monomer accumulates, and migration of the free valency takes place as a result of depolymerisation–polymerisation processes.

$E_d - E_{tr} \leq 5-6$ kcal mole^{-1}: i.e. the loss of radicals having the free valency in the middle of the chain would be due to decomposition reactions. This conclusion is supported by experiment: in poly(methyl methacrylate)[86], polystyrene[97], and other polymers of analogous structure loss is always accompanied by the ejection of products of low molecular weight, the quantity of which equals or exceeds the concentration of radicals [in polyalkenes the quantity of volatile products evolved at $T \leq T_{st}$ is smaller by factors of 10–1000 than in poly(methyl methacrylate)[113]].

Breakdown is followed by a series of further changes, leading to migration of the free valency and combination of the radicals. In poly(methyl methacrylate) the following reactions are possible[86]:

1. Breakdown of radicals:

$$-CXY-\dot{C}H-CXY- \longrightarrow -CXY-\dot{C}H_2 + CXY=CH-CXY-.$$

2. Depolymerisation with the separation of several monomer units.

3. Stabilisation

$$-CXY-\dot{C}H_2 + -CXY-CH_2-CXY- \rightarrow CXY-CH_3 + -CXY-\dot{C}H-CXY-$$

$$-CXY-\dot{C}H_2 + CH_2=CXY \rightarrow -CXY-CH_2-CH_2-\dot{C}XY;$$

4. Combination of mobile active radical $-CXY-\dot{C}H_2$ with fixed radicals $-CXY-\dot{C}H-CXY-$ or $-CH_2-\dot{C}XY$.

In polystyrene[97] decomposition is accompanied by the separation of the simple radicals $C_6H_5\dot{C}H_2$, $C_6H_5CH_2\dot{C}H_2$, etc., which diffuse into the interior of the polymer, and either combine with fixed radicals or abstract a hydrogen atom and are converted into saturated compounds—toluene, ethylbenzene, etc.

Breakdown always leads to migration of the free valency, which may occur as a consequence of construction of the ends of the disintegrated chain, depolymerisation, the formation and diffusion of simple radicals, etc. As a consequence of migration, radicals having the free valency in the middle of the chain are partly destroyed and partly stabilised, i.e. converted into a more stable form [in poly(methyl methacrylate) and polystyrene, for example, into radicals of the types $-CH_2-\dot{C}XY$ and $-CH_2-\dot{C}HX$]. The proportion of radicals lost

$$\omega = \frac{[R_0^{\cdot}] - [R_{st}^{\cdot}]}{[R_0^{\cdot}]} \qquad (21)$$

depends on the relative rates of combination and stabilisation. In poly(methyl methacrylate) $\omega \simeq 0.4$.[86,97]

Peroxy-radicals

In most vinyl polymers peroxy-radicals are lost in almost the same temperature range as are radicals having the free valency in the middle of the chain. The conversion of alkylated radicals of types (II) and (III) into the peroxide form

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot} \qquad (22)$$

is almost always equivalent to an increase in activity in hydrogen-transfer reactions

$$ROO^{\cdot} + HR_1 \rightarrow ROOH + R_1^{\cdot}. \qquad (23)$$

It would seem that repeated alternations of reactions (22) and (23) in the presence of oxygen should lead to migration of the free valency and loss of radicals[111]. Such a mechanism of migration represents an unbranched chain oxidation of the polymer. In most cases, however, the chain is relatively short, the number of oxygen molecules absorbed in the loss of one radical being respectively 5, 3–6, 3–7, and 1.5 in polyethylene[106], polypropylene[96], poly(vinyl chloride)[94,96], and poly(methyl methacrylate)[97]. Thus this mechanism, though at first glance extremely simple, cannot be regarded as the principal or only mechanism of migration of the free valency in the presence of oxygen.

A peculiar feature of reaction (23) is that abstraction of a hydrogen atom results in the formation of radicals having the free valency in the middle of the chain, whose stability is roughly the same as that of the ROO• radicals. Consequantly reaction (23) causes further migration of the free valency by a mechanism which is specific for a given polymer. In polyalkenes this may be stepwise transer of the free valency[94,107]. In poly(methyl methacrylate) and polystyrene, radicals having the free valency in the middle of the chain break down with the separation of products of low molecular weight[97]. The migration is accomplished quite rapidly—more rapidly than oxidation of the alkylated radicals formed—and the next oxygen molecule adds to the already stabilised decomposition products. Therefore many similar rules apply to the loss of peroxy-radicals and of radicals having the free valency in the middle of the chain[97] (volatile products having the same composition, same stability, etc.).

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Of the two parts of the review the first—the e.s.r. spectroscopic section—will probably leave a more complete impression than the second, more chemical part. The non-equivalence of these sections reflects the present-day state of research into the structure and the properties of polymer radicals.

One of the chief tasks of the e.s.r. spectroscopy of polymer radicals is to study the relation between the structure of radicals and their e.s.r. spectra. Work in this field is still far from complete, but considerable progess has been made during the past few years. Two or three years ago tens of investigations were devoted to deciphering a single spectrum, but now the possibility is already being discussed of predicting the hyperfine structure of the spectra due to very simple radicals.

Research on elementary radical reactions in solid polymers is at an earlier stage of development: theoretical concepts have not yet been established, and there is no generally accepted view on the formal kinetic laws, while many conclusions must for the present be compared with results for analogous reactions in liquid and gaseous phases. However, estimates have already appeared for the kinetic constants of radical reactions in the solid phase, and the elementary mechanism of complicated processes, such as the migration and destruction of radical states, oxidation, etc., is being discussed. It may be hoped that in the near future more serious generalisations will appear, with conclusions on the nature of the reactions undergon by radicals in solid polymers.

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Institute of Chemical
Physics, USSR Academy
of Sciences, Moscow

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Progress in the Study of the Degradation and Stabilisation of Siloxane Polymers

T.N.Balykova and V.V.Rode

The most recent achievements in the study of the degradation and the stabilsation of polyorganosiloxanes, including those containing other atoms in the chain, are surveyed. The effect of polymer structure on their thermal stability is examined, and the part played by catalytic impurities in developing processes of thermal and thermo-oxidative degradation is shown. Known schemes for the decomposition of polyorganosiloxanes are discussed. Data are given on methods of stabilising siloxane polymers. The list of references contains 141 items.

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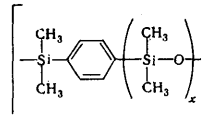
1. INTRODUCTION

The chemistry of monomeric and polymeric organosilicon compounds has made great advances during recent years. Polyorganosiloxanes possess several extremely important properties, in virtue of which they have found widespread and effective application in electrical engineering, radio engineering, and the coal, rubber, aircraft, and other industries. Such important properties of siloxane polymers as their resistance to the action of moisture, heat, cold, ultraviolet rays, oxygen, and ozone, their slight change in viscosity and modulus of elasticity with temperature, and their high dielectric properties are largely determined by the character of the siloxane chain and the organic radicals attached to the silicon atom. Polyorganosiloxanes can be regarded as occupying an intermediate position between organic and inorganic polymers. Several monographs[1-7] on the synthesis and investigation of the properties of siloxane polymers have been published during the thirty years since the appearance of the first papers in this field. However, problems of thermal and thermo-oxidative degradation and of stabilisation are inadequately dealt with in these works. The present review summarises available published data on the aging and stabilisation of polyorganosiloxanes published up to June 1967.

2. EFFECT OF THE STRUCTURE OF POLYORGANOSILOXANES ON THEIR THERMAL STABILITY

The spiral structure of the molecules of polyorganosiloxanes containing 3–6 silicon atoms in a loop of the spiral creates favourable conditions for the formation of rings. It is obviously for this reason that the decomposition of polydimethylsiloxane is accompanied by cleavage of the silicon–oxygen bond and separation of cyclic products of low molecular weight without appreciable disturbance of the silicon–carbon bond. It is therefore supposed[1,2] that the decisive factor in the thermal degradation of linear polysiloxanes is not the difference in energy between silicon–oxygen and silicon–carbon bonds but the spiral structure of the molecules.

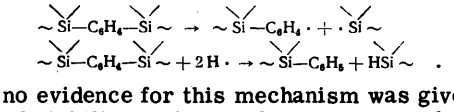
Enlarging the organic radicals attached to the silicon atoms diminishes the tendency of the polymer chain to coil into a spiral, so that depolymerisation of polydiethylsiloxane takes place with considerably greater difficulty and at a higher temperature than that of polydimethylsiloxane[2]. Polymers containing silaphenylene links possess fairly high thermal stability[8-14]. Those having the following structure



(I)

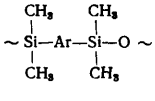
where $x = 1-4$, are considerably more thermostable than are ordinary polydimethylsiloxanes[14]. The maximum rate of loss of weight (1.4–1.9% min^{-1}) during the pyrolysis of such polymers is observed at 520–540°C, whereas with polydimethylsiloxane the maximum rate (2.1% min^{-1}) is already observed at 420°C. The polymer in which $x = 1$ proved to be the most stable.

It was assumed that cleavage of the silaphenylene link at temperatures above 450°C comprised the following reactions



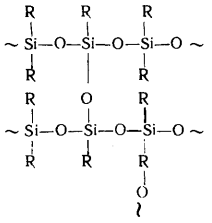
However, no evidence for this mechanism was given. The high thermal stability of these polymers was explained by the greater difficulty of breaking the silicon–carbon than the silicon–oxygen bond in polydimethylsiloxane.

Goldovskii, Kuz'minskii, and their coworkers[11] obtained comparative data on the thermal stability of the polymers



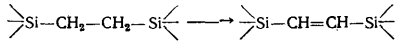
where Ar represents a *pp'*-phenyleneoxyphenylene or a *p*- or *m*-phenylene radical, and also data on the effect of small numbers of these units introduced into the chain of polydimethylsiloxanes. The polymer containing diphenyl oxide units proved to be the most stable, its decomposition temperature being 100 deg above that of polydimethylsiloxane, while the least stable polymer was one containing *m*-phenylene links. The introduction of up to 3 mole% of silarylene units into the chain of polydimethylsiloxanes has no significant effect on their thermal stability[11]. However, there are indications[13] that polymers containing biphenylylene and naphthylene bridges in the chain are stable even at 600°C, and will yield very strong thermostable films whose properties remain unchanged up to 400°C.

The thermal stability of polyorganosiloxanes is substantially influenced also by the structure of the polymer chains. Rupture of one silicon–oxygen bond is sufficient for the cleavage of linear macromolecules, but with polymers having a three-dimensional structure it is necessary to rupture siloxane bonds at two or even three points. Therefore the thermal stability of the latter is considerably higher than that of linear polymers. For example, polymers having the branched structure



undergo hardly any changes when heated in a vacuum at 550°C for 16 h.[15]

The thermal stability of polyorganosiloxanes is improved by vulcanisation with peroxides or γ-rays, the radiation products being the more thermostable[16–18]. The difference in thermal stability between these two types of vulcanised products is explained by a difference in the character of the cross-links[19]. In peroxide vulcanisates cross-linking is effected mainly by methylene bridges or silicon–silicon bonds. In radiation vulcanisates $Si-CH_2-CH_2-Si$ links are mainly formed, by the recombination of $Si-CH_2^{\cdot}$ free radicals. The thermal stability of radiation vulcanisates is higher because carbon–carbon bonds are more stable than silicon–carbon or silicon–silicon bonds, and also because at high temperatues a certain number of double bonds can be formed in the rubbers by the reaction



The rupture of cross-linking double bonds is difficult, and prevents degradation.

It is characteristic of thermal oxidation that the oxygen acts directly only on the organic groups attached to the silicon atom. The structure of the groups framing the main chain exerts a strong influence, of course, on the thermal stability of the polyorganosiloxanes. As the alkyl side-chain becomes larger, the thermo-oxidative stability becomes lower. Thus polydimethylsiloxanes[15] begin to oxidise appreciably at 200°, polydiethylsiloxanes at 138°, and polydibutylsiloxanes at 120°C.[20] Replacing the methyl by vinyl groups also somewhat lowers thermal stability[21,22].

On the other hand, replacing the methyl by phenyl groups considerably improves the thermo-oxidative stability of polyorganosiloxanes[23–25]. Thus at 350°C the loss in weight of polyphenylsiloxane is insignificant, but after heating at 450°C for 24 h about 3.7% of carbon and 0.76% of hydrogen remain in it[3]. The enhanced stability of polyphenylsiloxanes is explained[26] by the screening effect of the phenyl groups on the siloxane bond. The introduction of one chlorine atom into the phenyl group has no substantial effect on the thermal stability of polyphenylmethylsiloxanes, but with two or more chlorine atoms the thermal stability falls[27]. Thus the temperature at which decomposition begins drops from 357° for the unchlorinated polymer to 312°C for a polymer containing four chlorine atoms in the phenyl ring[28].

In polydimethylphenylsiloxane containing methyl-3,3,3-trifluoropropylsiloxy-groups processes of rearrangement of the siloxane link occur at an appreciable rate, which increases with increase in the content of these groups[29]. Half-decomposition times have been calculated[24] for polyorganosiloxanes containing various framing groups. Depending on such groups, these polymers can be arranged in the sequence

$$C_6H_5 > ClC_6H_4 > Cl_3C_6H_2 > Cl_2C_6H_3 > CH_2{=}CH > CH_3 > C_2H_5 > C_3H_7 > C_4H_9$$

according to their resistance to thermal oxidation.

Sobolevskii and Nazarova[30] investigated whether the thermal properties of organosiloxanes are determined by the arrangement of methyl and phenyl groups in the chain or by the overall CH_3/C_6H_5 ratio, and concluded that the principal thermal properties of these polymers are almost identical at similar values of the ratio, whether their structure is regular or irregular. The thermo-oxidative stability of polyorganosiloxanes is enhanced by the introduction of aromatic rings into the main chain[9–11]. The temperature at which a polydimethylsilarylene begins to be oxidised is 40–60 deg higher than with ordinary polydimethylsiloxanes, while the rate of elimination of methyl groups is smaller by factors of 5–8.[11] The introduction of *m*-phenylene links into the siloxane chain has an especially large effect on resistance to oxidation.

The thermal stability of polyorganosiloxanes containing arylene units in the main chain is slightly better than that of the corresponding polymers containing framing aryl groups when the ratio of these groups to the total number of siloxane units is the same[9].

A weak site in polymethylphenylsiloxanes is found at their terminal trimethylsiloxy-groups, which determine the thermo-oxidative stability[31]. Replacement of these groups by triphenylsiloxy-groups leads to an improvement in the thermal stability of the polymer of 50 deg.

The processes which occur during the thermo-oxidative degradation of polyorganosiloxanes depend in considerable measure on the structure of the polymer. These polymers can be either linear, branched, network, cyclolinear, or cyclo-network. The rate of elimination of organosilicon compounds is considerably lower when a three-dimensional polyorganosiloxane (R/Si = 1) is heated than in linear polymers, as is also the case in the absence of oxygen. Thus heating polydimethylsiloxane in air at 400°C for 3 h produces a loss of weight of 57%, whereas polymono-organosiloxanes under hardly any loss in weight up to 450°C.[2]

In the thermal oxidation of polyorganosiloxanes of three-dimensional cyclic structure $(RSiO_{1.5})_n$ having rings of different but definite size, it was found that polydimethylsiloxanes containing an even number of units in the ring are degraded more slowly than those with odd rings[32]. This is observed both at 350°C, when decomposition of the polymer is not yet complete, and also at 400°C. This effect of the parity factor was explained by the presence of polar forces, the strengthening of which was accompanied

by increased density of packing, so that the polymer became less subject to degradation. With polyethylsiloxane, however, the opposite phenomenon is observed: a polymer containing an odd number of units in the rings is the more heat-resistant.

The more frequent the cross-links in polyorganosiloxanes the greater their resistance to thermal oxidation, even if the total functionality of the polymer is lower[33]. Thus polymers of the type T–D–D–T are more thermostable than are T–D–D–D–T–T and T–T–D–D–D–D–T–T, where T and D represent tri- and di-functional units.

The considerably lower thermal stability of linear polyorganosiloxanes than of the three-dimensional polymers is explained by many authors on the one hand by the spiral form of the linear molecules, which creates favourable conditions for the cleavage of chains with the formation of cyclic products, and on the other hand by the fact that detachment of a chain segment in a linear molecule involves rupture of a smaller number of bonds[2–4].

The rate of oxidation of methyl groups also diminishes as the R/Si ratio falls[24,34].

From all the above discussion it follows that, to obtain the most thermostable polyorganosiloxanes, three-dimensional polymers must be synthesised containing arylgroups in the side-chains or in the main chain. Unfortunately, however, this is not always acceptable, since such polymers are less elastic.

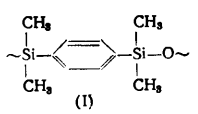
3. COMPOSITION OF DEGRADATION PRODUCTS OF POLYORGANOSILOXANES

The composition of the thermal degradation products of polydimethylsiloxanes was first studied by Patnode and Wilcock[35], who found that, in an atmosphere of nitrogen, polydimethylsiloxane decomposes at 350–400°C to form the following percentages of cyclic compounds of low molecular weight

$[(CH_3)_2SiO]_3$	44
$[(CH_3)_2SiO]_4$	24
$[(CH_3)_2SiO]_5$	9
$[(CH_3)_2SiO]_6$	10
above the hexamer	13

Compounds having a complicated cyclic structure were identified[36] among the products of the thermal degradation of three-dimensionally cross-linked polyorganosiloxanes.

When the silarylene polymer



(I)

was heated to 500°C (at a rate of 2.7 deg min^{-1}) and kept at that temperature for 3 h, hydrogen, methane, ethane, and ethylene were detected among the gaseous pyrolysis products, as well as dimethylsilane and tetramethyldisiloxane. The liquid products contained Si–H or Si–C_6H_4–Si groups. Elementary analysis, determination of the molecular weight, and spectroscopic data showed the solid reaction product to be a dimer. Thus the pyrolysis products indicate that degradation of the polymer chain takes place solely by rupture of silicon–phenylene bonds[14].

Thermo-oxidative degradation also yields solid and liquid products, among which a cyclic trimer—hexamethyltrisiloxane—predominates[19,24], but polymethylcyclosiloxanes of higher molecular weight are also present. Cyclic difunctional compounds mainly separate in the degradation of polymethylphenylsiloxane rubber[37].

Thus the thermo-oxidative degradation of polydiorganosiloxanes, like the thermal process, involves rupture of the silicon–oxygen bond to form cyclic products of low molecular weight. Substances indicating oxidation of organic side-chains are also found among the products of thermo-oxidative degradation. Thus in 1947 Atkins and Murphy[38] detected formaldehyde and formic acid among the thermal oxidation products of polydimethylsiloxanes. Subsequently carbon monoxide, carbon dioxide, methanol, water, and hydrogen have also been detected[21,24]. Furthermore, methane has been found in the oxidation of a siloxane rubber at 400°C.[39] These products are formed as a result of the oxidation and detachment of organic radicals.

As a consequence of the great resistance of phenyl groups to oxidation, only degradation of the main chain takes place in polyphenylsiloxanes up to 300–400°C.[21] From elementary analyses of polydi(and mono)methylsiloxanes which had been oxidised in air at 250–300°C Andrianov and Sokolov established[24] that the atomic ratio of hydrogen to carbon remained approximately 3 until a considerable degree of oxidation had occurred: i.e. methyl groups were split off during oxidation. Vinylated polymers form an exception among the polyorganosiloxanes. The vinyl groups do not split off from the main chain, since after oxidation at 200°C the carbon, hydrogen, and silicon contents of the residue do not differ appreciably from those of the original polymer. Infrared-spectroscopic data showed that the volatile products were siloxanes of low molecular weight, of the same composition as the initial material but containing carboxyl groups[21].

The oxidation of polyorganosiloxanes is accompanied by cross-linking: the viscosity of soluble polymers increases, and with further oxidation a gel is formed[39,21,23]; insoluble polymers show a rise in their glass point[40]. The fact that the rate of increase of the viscosity increases with increase in the oxygen content[38] suggests that the cross-linking is actually due to the action of oxygen. Electron-microscopic examination of the changes in a polydimethylsiloxane film when heated in air at 200°C show a coarsening of the macromolecular aggregates[41]. This is probably explained by cross-linking of the polymer chains under these conditions. Since the infrared spectra contained no bands corresponding to silicon–silicon bonds, it was assumed that the bridges between the chains were formed by siloxane bonds at the points of detachment of methyl groups[3]. The mechanism will be discussed below. Andrianov and Sokolov showed[24] that, as long as the molar ratio H/C = 3, approximately one oxygen atom replaces every two methyl groups eliminated. At the present time most scientists consider that the cross-links formed in the oxidation of polyorganosiloxanes are siloxane bonds[1,3,5,39], but inadequate grounds are given for this view.

4. THERMAL DEGRADATION OF POLYORGANOSILOXANES

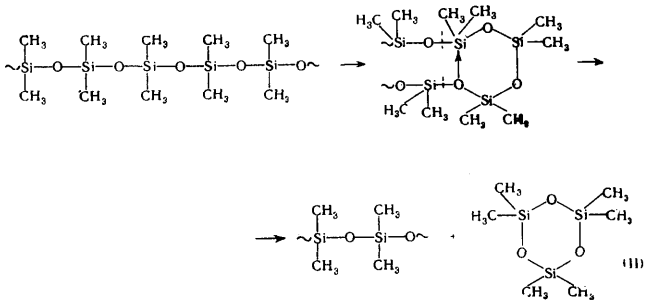
A limited amount of work has been done on the kinetics of the depolymerisation of polyorganosiloxanes in the absence of air. Andrianov et al.[42] investigated the kinetics of thermal degradation from the variation in the viscosity and the weight of the polymer. A striking fact is that the intrinsic viscosity begins to rise before loss of weight starts: with polydimethylsiloxane the latter is observed at 220°C, whereas the intrinsic viscosity has already begun to increase at 170°C. As the temperature

rises the viscosity increases, reaches a maximum value at 300°C, and then diminishes with further rise in temperature. The increase in viscosity was regarded as probably due to increase in the molecular weight of the polymer as a result of polycondensation involving the terminal hydroxyls. Above 220°C the structural changes begin to be accompanied by thermal breakdown of the polymer with the separation of products of low molecular weight which is responsible for the loss in weight; above 300°C depolymerisation becomes the dominant process.

In the initial stage the thermal degradation conforms to a first-order kinetic equation, but as the extent of conversion increases to 30–35% the order of the reaction increases slightly. The explanation given for this increase is that, together with the formation of cyclic compounds resulting from depolymerisation, other processes occur, leading to structural changes in the polymer.

Until recently, only fragmentary data of tentative character were available on the mechanism of the thermal decomposition of siloxane polymers. It was found in particular that linear organosiloxanes break down in the ionisation chamber of a mass spectrometer at 150–200°C to form dialkylsiloxanes[43,44]. From this it was suggested that the depolymerisation of linear organosiloxanes involves an intermediate stage in which dialkylsilanes are formed, these polymerising to cyclic products. However, in this case rupture of the siloxane bonds occur under the ionising action of the chamber of the mass spectrometer, not by the action of heat on the polymer under conditions of thermal degradation.

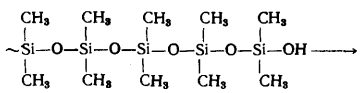
A mechanism has also been suggested for the formation of cyclic products in which depolymerisation of polydimethylsiloxane produces an intermediate compound which lowers the energy barrier to the rupture of silicon–oxygen bonds:

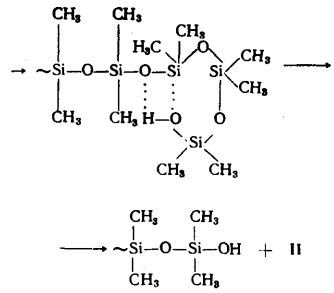


(III)

Unfortunately, no experimental data were given to support this mechanism.

The dependence of the depolymerisation rate constant on the degree of polymerisation of polydimethylsiloxanes was found to correspond to initiation of this reaction by terminal groups[45,46]. Examination of the thermal degradation of polydimethylsiloxane containing various kinds of end-groups showed that the rate of depolymerisation is diminished considerably when the terminal hydroxyls are replaced by methyl groups or by groups containing copper, iron, or titanium atoms. The following scheme was therefore proposed for the depolymerisation of polydimethylsiloxane:





Formation of an activated transition complex is favoured by the presence of hydroxy-groups and a spiral structure of the siloxane chains. The proposed mechanism is supported by the fact that, with decrease in the degree of polymerisation of the polydimethylsiloxane, the experimental values of the effective activation energy of depolymerisation (14–16 kcal mole^{-1}) approach the calculated energy of formation of the activated complex.

With increase in molecular weight, random cleavage of the chain plays an increasingly important part, so that the activation energy increases (to 32 kcal mole^{-1}).[40]

On the basis of thermogravimetric results Andrianov et al.[72] put forward a two-step mechanism of the degradation of polyorganosiloxanes. The first stage of decomposition (loss in weight 15–20%) has an activation energy of around 40 kcal mole^{-1}, and was regarded as involving the degradation of polydimethylsiloxane chains having terminal hydroxyls, with the formation of a network structure. In the second stage the polymeric networks undergo thermal cleavage, as indicated by the high activation energies of this process (60–80 kcal mole^{-1}).

5. THERMO-OXIDATIVE DEGRADATION OF POLYORGANOSILOXANES

Much work has been done on the kinetics of the thermal oxidation of polyorganosiloxanes. A kinetic investigation has been made of the separation of formaldehyde, the separation of formic acid, and the change in viscosity at low degrees of oxidation of a polydimethylsiloxane rubber[38], and also of the loss in weight of the polymers[21]. The time variation in the quantity of formaldehyde and formic acid which separated in a stream of oxygen at 200°C was approximately linear. However, the process cannot be assessed from these kinetic results, since formaldehyde and formic acid are not the only products of the oxidation of methyl groups. Furthermore, these results related only to the initial period, and differed markedly for different specimens, the difference in whose compositions was not indicated. Results for the variation in viscosity also cannot be applied as a quantitative measure, since they were not converted to the number of cross-links formed. It is impossible to assess the course of oxidation by means of curves for the loss in weight, since the latter is caused not only by the oxidation of methyl groups but also by breakdown of the main chain.

A characteristic feature of the kinetics of the decrease in weight of polymonomethylsiloxanes and other polymonoorganosiloxanes[24,37,39] is the sharp decrease in rate of loss of weight after the initial period. Approximately half the loss takes place in the first hour. Since the weight losses in such polymers are due merely to oxidation of lateral groups (when these polymers are heated, no separation of

products of low molecular weight is observed up to 400–500°C), these results enable the course of oxidation of the polymer to be assessed. A rapid decrease in the rate of the process after the initial period was observed by Scala et al.[21] also in a kinetic study of the absorption of oxygen by a polydimethylsiloxane resin at 250°C. Heating a phenylsiloxane rubber[37] in air established that the rate of decrease in weight obeys the empirical equation

$$\frac{df}{dt} = ke^{-k_1 f}$$

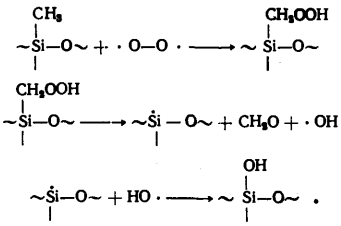
where f is the loss in weight of the specimen, and k and k_1 are constants. It was found that removal of the strongly oxidised upper layer of the specimen led to an increase in the rate of loss of weight. The explanation given was that, owing to cross-linking during oxidation, the diffusion of volatile products was impeded, and their concentration in the specimen increased. The activation energy of the thermo-oxidative degradation of a phenylsiloxane rubber was 22.2 kcal mole^{-1}.

Scala et al.[39] investigated the effect of the air pressure on the thermal oxidation of polymethylphenylsiloxanes (at 700, 600, 500, 300, 100, and 50 mmHg). Comparison of the final losses in weight in air and in argon showed that the purely thermal effect was responsible for 70% of the losses over the pressure range 700–300 mmHg, and for 92% at 50 mmHg of air. From the variation in the ratio of the quantity of gaseous compounds formed to the amount of oxygen absorbed it was suggested that oxidation takes place by different mechanisms at air pressures of 700–300 and below 300 mmHg.

While studying the relaxation of stress in preoxidised specimens of a polydimethylsiloxane rubber, Kuz'minskii and Goldovskii established[47] that the rate of relaxation diminishes with increase in density of the three-dimensional network. Such a relation is observed if cleavage takes place predominantly in the main chain, not at cross-links. The results given in this paper suggest that some kind of active groups accumulate in the polymer during oxidation. The kinetic curves representing the separation of organosilicon compounds of low molecular weight are S-shaped, which indicates the presence of a period of autocatalysis[48], also associated with accumulation in the polymer of active centres capable of breaking down the main chain. The rate of separation of these compounds increases for a certain time, after which it begins to fall, probably owing to the formation of cyclic segments, which impede further cleavage of the siloxane chain.

Thus oxygen does not act directly on the siloxane bond, but is responsible for the formation of active groups which accelerate depolymerisation. However, the mechanism of such acceleration has not been elucidated. It has merely been suggested that the process is hydrolytic in character, and that the active groups influencing cleavage of the main siloxane chain are Si–OH groups[49–51].

In view of the structure of polydimethylsiloxane, the mechanism of the oxidation of the lateral radicals should have much in common with the mechanism of the oxidation of organic polymers such as polypropylene. It has been suggested that oxidation of the side-chains involves formation of hydroperoxides[24] by a mechanism similar to the oxidation of polypropylene[52–55]. Andrianov and Sokolov[24] consider that oxygen attacks a carbon atom attached to silicon in the polymer molecule; a hydroperoxide is first formed, and rapidly decomposes with the separation of formaldehyde and the HO· radical, the latter adding to the silicon atom:



Condensation of the polymer molecules then takes place by means of the hydroxysilyl groups. The thermal decomposition of formaldehyde yields carbon monoxide and hydrogen, and its oxidation produces carbon dioxide and formic acid.

An analogous mechanism was suggested by Scala[39], who regards the process as a chain reaction;

chain initiation: $RCH_3 + O_2 \rightarrow RCH_2^{\cdot} + HO_2^{\cdot}$

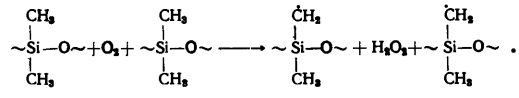
chain growth:
$RCH_2^{\cdot} + O_2 \rightarrow RCH_2O_2^{\cdot}$
$RCH_2O_2^{\cdot} + RCH_3 \rightarrow RCH_2O_2H + RCH_2^{\cdot}$
$RCH_2O_2H \rightarrow RCH_2O\cdot + HO\cdot$
$RCH_2O\cdot \rightarrow R\cdot + CH_2O$

where R is a polymer radical having its free valency on a silicon atom.

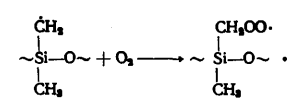
It has been established[56] that the rate at which methyl groups are split off increases with increase in the thickness of a film. The rate of oxidation increases up to a certain thickness, after which it decreases. Thus an "optimum" thickness corresponds to each temperature: 0.3, 0.75, 2.5, and 4 mm at 300°, 270°, 250°, and 230°C respectively.

The increase in the rate of oxidation is explained by the catalytic action of the oxidation products (perhaps formaldehyde), but when the optimum thickness is reached, delays involved in the diffusion of oxygen overlap the first factor. From these conclusions it can be assumed that the oxidation of methyl groups has a chain mechanism. Formaldehyde causes branching of the catalytic chain in the thermal oxidation of the side-groups in polydimethylsiloxane[57]. A chain mechanism is supported also by the sharp decrease in rate of oxidation produced by introducing antioxidants, e.g. 0.5–1.0 wt.% of di-2-naphthyl-*p*-phenylenediamine, into the polymer[56]. An analogous phenomenon is observed when such compounds as titanium dioxide and powdered silica gel are added to the polymer[49].

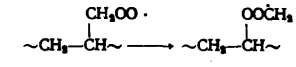
Oxidation is said[57] to be initiated by the abstraction of a hydrogen atom from a methyl group by an oxygen molecule:



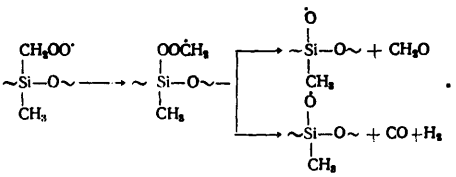
As in the oxidation of hydrocarbons, radicals with a free valency on a silicon atom should react preferentially with oxygen:



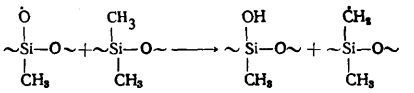
The most probable reaction of the peroxy-radical is its rearrangement by analogy with that of a peroxy-radical of polypropylene[53–55]:



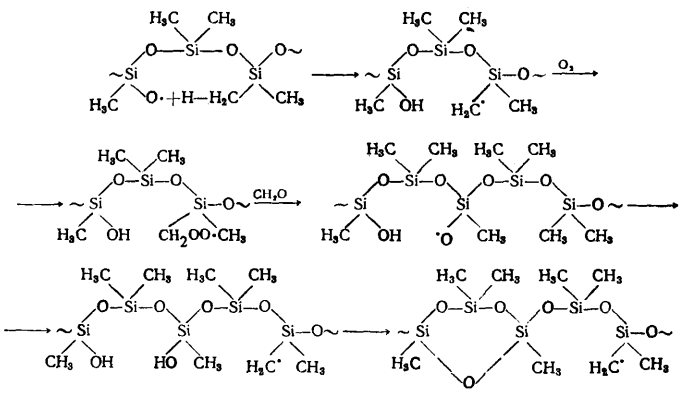
This reaction would be still more probable in polydimethylsiloxane, since its methylene C–H bonds are more stable than those in polypropylene: i.e. the $\geqslant SiCH_2OO^{\cdot}$ radical is more active than $\geqslant C-CH_2OO^{\cdot}$. In the authors' opinion the peroxy-radical undergoes the following reactions[48]



The resulting radical reacts with a methyl group of the same or a neighbouring molecule to form a hydroxy-group:



Since the number of methyl groups split off during the initial period of oxidation considerably exceeds the number of intermolecular siloxane bonds formed, the authors suppose that the start of oxidation involves predominantly the formation of intramolecular siloxane bonds:



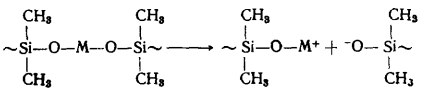
6. EFFECT OF CATALYTIC IMPURITIES ON THE THERMAL STABILITY OF POLYORGANOSILOXANES

Polydimethylsiloxane, when free from acidic or basic impurities, is extraordinarily stable at relatively high temperatures. In most cases polydimethylsiloxanes are obtained by the anionic polymerisation of cyclic compounds, and the presence of catalysts in them is inevitable. Several papers have shown that the presence of polymerisation catalysts lowers the thermal stability considerably.

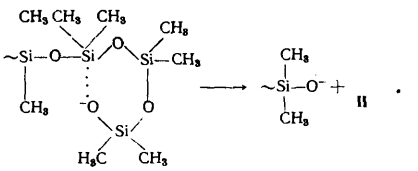
The thermal stability of polymers is greatly dependent on the type of catalyst used for their preparation. Thus the losses in weight of the SKTV brand of siloxane rubber, produced with an acid catalyst, are 25% on heating in a vacuum at 350°C for 2 h, but when an alkaline catalyst is used the same loss in weight is already observed at 265°C.[58] Under conditions of thermal oxidation, polymers prepared with acid catalysts possess diminished thermal stability, since acids accelerate the oxidation of the side-groups. Kučera et al.[59] studied the depolymerisation and oxidation of the lateral groups in polydimethylsiloxanes prepared by anionic polymerisation and neutralised with several acidic agents. The smallest losses in weight were observed in a polymer stabilised with benzoic acid, whereas carbon dioxide had hardly any stabilising effect. The greatest resistance to depolymerisation is exhibited by a mixture of polymers obtained with caustic potash and sulphuric acid as catalysts: depolymerisation of this mixture is completely suppressed at 350°C and 10 mmHg. However, the additives do not protect the polymer from thermo-oxidative degradation: the mixture of polymers obtained with the two catalysts undergoes change in structure especially rapidly.

The two polymers obtained with potassium hydroxide and tetrabutylphosphonium hydroxide as catalysts undergo similar thermal degradation, but the latter polymer undergoes great changes in the course of thermo-oxidative degradation. This is due to breakdown of the catalyst with the formation of acidic products, which accelerate the oxidation[60]. It has been established[59] that the rate of oxidation is a function of the dissociation constant of the acid used as catalyst.

Lewis[61] observed a sharp increase in the rate of decomposition of the polymer after the loss in weight had reached 20%, and assumed this acceleration to be caused by certain components, present in the polymer, which catalysed the process of thermal decomposition. Spectral analysis established the presence of metallic impurities in the polymer (0.05% of barium, 0.01% of lead, 0.0005% of silver, 0.005% of aluminium, and 0.001% of magnesium). Since the concentration of these impurities was too small to catalyse the fission of a silicon–oxygen bond, they were assumed to react with the ends of the chain or to split "abnormal bonds" (silicon–silicon or oxygen–oxygen). This involved formation of so called "live" active centres, which accelerated depolymerisation[61,62]. The polymer molecules underwent dissociation at the point of incorporation of the impurity atom:

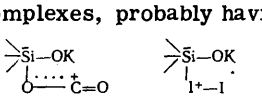


the resulting ions causing depolymerisation with the formation of volatile cyclic products of low molecular weight:



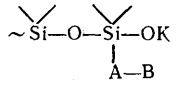
The rate of depolymerisation has been shown to be directly proportional to the square root of the concentration of active centres[63] and to increase with rise in temperature[59].

Several methods have been described for deactivating the active centres, such as the use of thermolabile catalysts, rinsing catalytic impurities out of the polymer, or else neutralising them. Kučera et al.[60] noted that the thermal stability of polydimethylsiloxanes was improved by the introduction of carbon dioxide or iodine. They assumed that these substances form with the active centres relatively stable complexes, probably having the structure



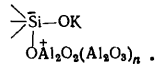
The carbon dioxide complex is stable only up to 150°C. The iodine complexes are considerably more stable, probably because of breakdown initially with the formation of potassium hypoiodite, which then disproportionates into the iodide and the iodate. Both the latter compounds are inert towards the siloxane bond, and neither catalyses the oxidation of methyl groups.

References have been made to the possible formation of stable complexes of the active centres with phenol, anisole, diphenylamine, and other compounds[64]. The stability of a complex, which can be represented by the general formula

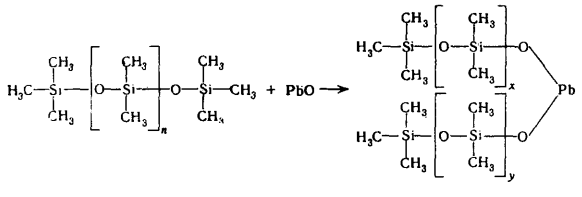


(where A is an electronegative group (oxygen, a halogen), while B is a hydrocarbon group or a metal atom), is determined by the nature of the donor and the type of atom or group combined with it.

Several papers[23,38,60] have dealt with the effect of metals and their oxides, employed for the polymerisation of siloxanes, on the thermal and thermo-oxidative stability of these polymers. Investigation of polymers contaminated with the oxides—ZnO, TiO_2, CdO, MgO, Fe_2O_3, Al_2O_3, BeO, SiO_2, etc.—showed the stabilising effect of these compounds to be very small. However, alumina and beryllium oxide are capable of completely suppressing depolymerisation for a very short time[60]. Only oxides with cations of small radius are able to form complexes with the active centres, which, perhaps, have the structure

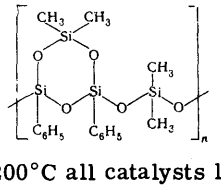


An investigation was made of the action of metals (tin, antimony, copper, lead, aluminium, nickel, selenium, silver, tellurium, zinc, and iron) on the thermal and thermo-oxidative stability of polydimethylsiloxane and polymethylphenylsiloxane. Lead and tellurium accelerated gel formation and the evolution of volatile products, but the other metals had no significant effect[23,38]. It was suggested[38] that lead oxide ruptures the chain under the influence of heat, and then reacts with the fragments to form larger fragments:

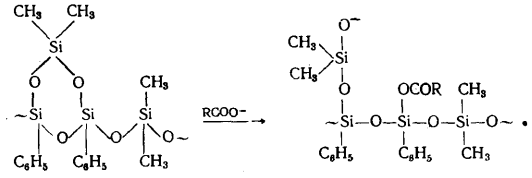


This compound is unstable, and decomposes into smaller fragments. This hypothesis is supported by the turbidity of solutions of the polymer in the presence of lead and tellurium.

Since siloxane polymers are often used as protective coatings and lacquers, it is interesting to examine the action of various pigments and hardening and drying catalysts on the thermal degradation. Andrianov and Fromberg[65] investigated the effect of drying accelerators for varnish films on the heat-resistance of a polymer having the cyclolinear structure



It was found that at 200°C all catalysts lower the heat-resistance of the coatings to roughly equal extents, although the naphthenates of zinc, cobalt, and magnesium have a rather stronger effect. The catalysts are supposed to promote rearrangement of the siloxane chains accompanied by opening of the rings and their recombination, which leads to the formation of cross-linked structures:



The mechanism of degradation varies with the chemical nature of the catalyst. Zinc naphthenate promotes only cleavage of the main chain, but does not affect oxidation of side-groups; whereas lead naphthenate catalyses both oxidation and the cleavage of the main chain. Among pigments (oxides of titanium, chromium, and lead) only chrome yellow catalyses the process of oxidation at 400°C. The remaining pigments do not lower the thermal stability of the films[65].

Investigation of the effect of fillers (titanium dioxide and powdered silica gel) on the thermal oxidation of polydimethylsiloxane showed that, when the degradation products are removed from the sphere of reaction, fillers enhance the thermal stability; if volatile products are not removed, the fillers lower the thermal stability[66]. The authors explain this by the occurrence of hydrolytic processes in the polymer, caused by water adsorbed on the filler (~ 6%).

With the aim of enhancing the thermal stability and improving the mechanical properties of polyorganosiloxanes containing active centres, Berlin et al.[67] proposed subjecting these polymers to a preliminary heat-treatment at 350°C for 1 h. In their view[67] this process occurs by a radical mechanism and comprises the following reactions—degradation of the chains at the weakest bonds and formation of macroradicals, chain transfer by the macroradicals, and cross-linking of the system by recombination of macroradicals with the formation of bonds which are quite stable under the conditions of heat-treatment.

Thus pigments, catalysts, and fillers have a substantial influence on the thermal stability of siloxane polymers. Although the action of these impurities on the silicon–oxygen bond can be quite easily diminished, it is considerably more difficult to inhibit their influence on the oxidation of the side-groups.

7. THERMAL AND THERMO-OXIDATIVE DEGRADATION OF POLYORGANOSILOXANES CONTAINING HETEROATOMS

In spite of the fairly high stability of polyorganosiloxanes, the limits of the fatigue life of these polymers no longer satisfy present-day demands of technology. In order to improve the thermal stability of polysiloxanes, polymers containing various heteroatoms in the chain have been prepared. Introduction into the siloxane chain of fragments the energy of whose bonds is considerably higher than that of the silicon–oxygen bond should increase the thermal stability of polyorganosiloxanes.

Polymers containing heteroatoms were first investigated by Andrianov. Great progress has now been made in the synthesis and investigation of several properties of polyorganosiloxanes containing titanium[68-74], tin[75,76], aluminium[77-80], boron[81-86], and other heteroatoms[87,88] in the chain. Chapters in monographs by foreign authors deal with these polymers[89-91].

The thermal stability of several such heterochain polyorganosiloxanes is far higher than that of polyorganosiloxanes themselves, and depends on the properties of the element introduced into the chain. Polymers containing titanium atoms in the chain exhibit the greatest thermal stability[92-96], and those containing boron and phosphorus atoms are hardly inferior to them. Thus the losses in weight in a vacuum at 450°C after 2 h were 12.7% and 19.3% in polyphosphaborasiloxanes and a polytitanasiloxane. A control specimen of polydimethylsiloxane containing no heteroatoms was completely degraded at 450–500°C.[92]

In an atmosphere of oxygen at 280°C the loss in weight of a phosphaborasiloxane polymer after 28 h was 12.2%, and that of a titanasiloxane polymer 2.47%. Polyborasiloxane retains its elasticity in air up to 390–400°C, polyphosphasiloxanes up to 400–420°C, and polyphosphaborasiloxanes up to 410–430°C; in a vacuum all these polymers remain elastic up to 540–570°C.[92]

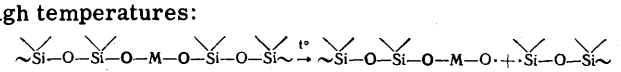
Thermogravimetric analyses indicate that the temperature at which polymethylstannasiloxane begins to decompose is 480°C, the corresponding temperatures for polyethylstannasiloxane and polyphenylstannasiloxane being 462° and 460°C.[97] Introduction of a germanium atom into the chain does not have a favourable effect on the thermal stability of a polyorganosiloxane[98].

The introduction of stannasiloxane copolymers into silicone rubber mixtures produces no improvement in the properties of the vulcanised products[99].

Adequate thermal stability is exhibited by polyphenylchromasiloxanes[100] (losses in weight at 300° and 450°C after 2 h were 12.23% and 43.2%), and also by polyorganoferrasiloxanes and polyorganoferra-alumasiloxanes[101]. Thus polyphenylferrasiloxane is highly stable and loses few volatiles at temperatures of 200–320°C.[101] A striking feature is the lack of correspondence between solubility and infusibility, which is associated with structural characteristics of these polymers.

On the basis of the elementary composition and the infrared spectra Andrianov and his coworkers[102-104] established that heterochain polyorganosiloxanes have a cyclolinear structure. The thermal stability of such rings is very great[103]. Differential thermal analysis indicates that ring-opening occurs at temperatures considerably higher than those at which the organic groups framing the inorganic part of the molecule are stable. The introduction of such groupings as B–O, P–O, P=O, Ti–O, Al–O, and Sn–O into the chain of polyorganosiloxane elastomers raises their thermal stability. It was suggested[95] that this was a consequence of the formation of supermolecular structures and the resultant orderliness of individual segments of the polymer chains.

Poddubnyi and Aver'yanov[105] explain the higher thermal stability of heterochain polyorganosiloxanes (420–430°C) compared with vulcanised SKT and SKTV silicone rubbers (370-380°C) by the inhibiting action of the metal heteroatom on chain radical processes of chain degradation at high temperatures:



where the more polar and stable M–O bond stabilises the Si–O bond and prevents chain cleavages at high temperatures from extending further than the heteroatomic unit. This hypothesis is consistent with the rupture of a silicon–oxygen bond in the immediate vicinity of a chain unit containing a heteroatom requiring the consumption not only of the energy evolved in its formation but also an additional quantity of energy equal to the difference between the internal energies of the radicals ≥Si· and ·O–M.[106]

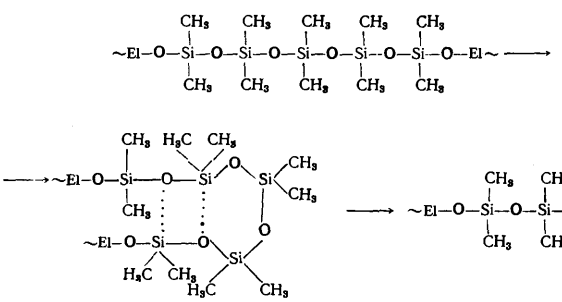
Andrianov[2] put forward the hypothesis that the enhancement of the thermal stability of the polymer by the introduction of heteroatoms into the chain was due to the possibility of forming coordinate bonds between the metal atoms and the oxygen of neighbouring chains.

It has also been established[41] that increasing the functionality and the coordinating power of the heteroatom leads to an improvement in thermal stability, while strengthening the basic power and diminishing the energy of the heteroatom–oxygen bond impair the thermal stability of heterochain polydimethylsiloxanes. Heteroatoms form the sequence—Al < B < Fe < Ti—according to their effect in improving the thermal stability of polymers.

Investigation of the thermal degradation of heterochain polyorganosiloxanes of regular structure containing aluminium, titanium, and boron atoms has shown that, as with polyorganosiloxanes themselves, the major part of the volatile products responsible for the losses in weight consists of hexamethylcyclotrisiloxane formed by cleavage of the silicon–oxygen bond. At high temperatures homolytic cleavage of silicon–hydrogen and carbon–hydrogen bonds also takes place, with the evolution of small amounts of hydrogen, methane, and ethane[41,107,108].

It has also been found[41] that the introduction of heteroatoms leads to a change in the mechanism of degradation. As a consequence of the presence of heteroatoms in the siloxane chain, the formation of an activated complex takes place according to the law of chance, not at the end-groups, as in linear polydimethylsiloxane. It is possible that depolymerisation at terminal groups ceases at the nearest heteroatom, and plays no part in the overall process.

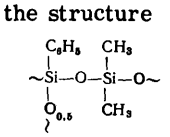
In view of the spiral structure of the siloxane chains, with three silicon atoms in a loop, formation of an activated complex followed by the elimination of cyclic products can be represented as



This hypothesis is supported by the good agreement between experimental and calculated values of the activation energy (29–33 and 32 kcal mole^{-1}) of formation of the transition complex shown. Formation of a transition complex involving a heteroatom is energetically unfavourable, since the activation energy will then considerably exceed 32 kcal mole^{-1}.

The thermo-oxidative stability of polyorganosiloxanes is strongly influenced by the introduction of a small quantity of polyorganoalumasiloxanes[109-111]. Thus the addition of polyphenylalumasiloxane to polydimethylpolyphenylsiloxane shifts the start of rapid decomposition under conditions of thermal oxidation from 400° to 450–500°C, while the loss in weight diminishes from 60% to 30%.[109]

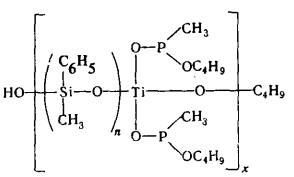
Andrianov and Petrashko[110] investigated the polyorganosiloxane having the structure



and its copolymers with polyphenylalumasiloxane containing 0.05%, 0.1%, 0.25%, and 0.5% of aluminium. Oxidation of the organic groups was found to be more vigorous in the copolymers than in the homopolymer. However, the losses in weight did not exceed the weight fraction of the organic portion, as in the case of polydimethylpolyphenylsiloxane. Hence no cleavage of the main chain takes place in the copolymers, and no organosilicon compounds of low molecular weight are evolved. The authors explain this by the formation in the copolymer of aluminium–oxygen coordinate bonds, which give rise to cross-linking and impede the formation of compounds of low molecular weight.

Thus the rate of thermo-oxidative degradation in the copolymers was found, on the one hand, to be increased in comparison with the homopolymer, owing to the more vigorous oxidation of the phenyl groups, and on the other to be decreased by cross-linking of the polymer. One or other process prevails depending on the aluminium content.

No published data are available on the effect of elements, introduced into the siloxane chain, on the mechanism of thermo-oxidative degradation, or on the composition and quantity of degradation products. Only in one paper is it noted that the thermal oxidation at 400°C for 4 h of poly-bis(organophosphinoxy)titana-methylphenylsiloxanes[112]

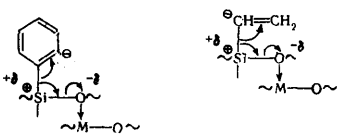


where n = 30, 50, 90, 120, 200, yields carbon dioxide together with liquid and solid organosilicon compounds of low molecular weight. With increase in the distance between the bisorganophosphinoxytitanoxane groups the quantity of cyclic products evolved diminishes, while the amount of carbon dioxide somewhat increases.

Very interesting work was done by Petrashko and Andrianov[96] on the effect of metal atoms in the siloxane chain on the rate of detachment of various organic groups during thermal oxidation. A polymer containing organosilasesquioxane units was investigated, whose thermal oxidation did not involve cleavage of silicon–oxygen bonds, so that the losses in weight could serve as a criterion of the stability of the organic radicals in this process. The rates of elimination of the radicals were compared by means of the dependence of the R/Si ratio on the time of heating. It was found that phenyl groups were eliminated considerably more vigorously than vinyl groups from the heterochain polymers, whereas the opposite relation was observed in the polyorganosiloxanes themselves. The intensity of detachment of a phenyl radical depends on the metal in the siloxane chain, increasing in the sequence Ti < Sn < Al. When the same metals are introduced into polydimethyl- and polydiethyl-siloxanes the stability of such polymers increases in the sequence Ti < Al < Sn.

The reason for the different effects of the organic radicals on thermal stability in polyorganosiloxanes and in the heterochain polymers is that phenyl and vinyl radicals exert a negative induction effect on the silicon atom. These radicals will therefore tend to attract a pair of electrons away from the silicon atom:

A bond of this type produces enhanced resistance to oxidation. When an Si–O–M bond is present in the molecule, the metal atom coordinates with the oxygen in the chain. The coordinate bond causes deformation of the electron sheath of the siloxane bond towards the oxygen atom, and the silicon atom acquires an induced positive charge +δ. The electron pair of the silicon–carbon bond shifts in the opposite direction to that caused by interaction of this electron pair with the π-bonds of the radical. This bond is thereby weakened:



Allyl radicals exert a positive induction effect on the silicon atom. The positive charge on the silicon atom induced by the metal–oxygen coordinate bond produces a displacement of the electron pair in the same direction as the induced effect of the radical. The stability of the radical is thereby raised.

8. STABILISATION OF POLYORGANOSILOXANES

The literature contains references to the possibility of stabilising polyorganosiloxanes, but there is no common approach to this problem. Since thermo-oxidative degradation comprises two independent processes—oxidation of side-groups and cleavage of the main chain with the evolution of volatile products of low molecular weight—all stabilisers which have been recommended can be provisionally divided into two groups—those which inhibit the oxidation of side-groups, and stabilisers which prevent rupture of the main chain in siloxane polymers.

Since the oxidation of side-groups in siloxane polymers has much in common with the oxidation of aliphatic groups in organic polymers (e.g. polypropylene), many authors suggest the use of antioxidants, which have proved to be very satisfactory for the stabilisation of polypropylene. The use of amines as stabilisers in the oxidation of a liquid polyethylsiloxane at 175–200°C increased the induction period of the increase in viscosity, the most effective at 200°C being phenyl-1-naphthylamine[113,114], aldol-1-naphthylamine[114], diphenylamine[115], Neozone D[113,115], and dinaphthylamine[115].

With liquid polydimethylsiloxane an increase in the duration of oxidation before a gel is formed at 200–400°C is observed[116] in the presence of antioxidants like aromatic amines and phenols. Since the latter may themselves decompose at high temperatures, the use of phenoxazine is recommended. The stability of polyorganosiloxanes can be improved[117] by means of amides (e.g. adipamide and urea). The use of antioxidants containing phosphorus is also advised, in particular phosphites of the type $P(OR)_3$ where R is an alkyl or an aryl group[118].

A solution of a polyorganosiloxane resin to which hardening catalysts have been added is stabilised against change in viscosity during storage by the addition of 0.5 wt.% of a

monohydric aliphatic alcohol containing four or more carbon atoms (e.g. 2-ethylhexanol).[119]

The thermal stability of polyphenylethyl- and polyphenylmethyl-siloxanes enamels at 250°C can be enhanced by the use of ethylated and butylated amine–formaldehyde resins[120].

To raise the stability of liquid polydimethylsiloxanes to gelatinisation under the influence of high temperatures it is recommended that 0.5–5 wt.% of bromine should be introduced[121]. The time of gelatinisation is then increased from 24 h for an unstabilised specimen to 1900 h for a specimen containing 0.9 wt.% of bromine (after degradation at 250°C).

Bass, Berlin, et al.[122] proposed stabilising siloxane polymers against thermo-oxidative aging by means of fused aromatic compounds, e.g. anthracene, previously in a vacuum at 300–450°C.

Substances capable of forming stable complexes with the active centres have been proposed as stabilisers to prevent cleavage of the main chain. Thus 0.06 wt.% of iodine[51] or 0.01–0.5 wt.% of partly dehydrated hydroxides of aluminium and iron[123] have been suggested; oxides of various metals—Fe, Al, Be, Si, Ti,[59] Co and Cu,[124] Ni, Mn, Cr[125]—are employed for the same purpose.

It has been observed that, when various compounds of metals are introduced into polyorganosiloxanes, the rate of depolymerisation falls considerably. Therefore most authors propose the addition of a great variety of metal compounds. Especially good results are given by compounds of transition metals, among which such salts have been suggested as the acetates and octanoates of iron[126], the naphthenates of lead[127], zinc, cobalt, iron, and manganese[65], the naphthenates and octanoates of indium and cerium[128]. The use has been proposed of the chlorides, acetates, fluorides, sulphates, nitrates, naphthenates, and oxides of such rare-earth metals as lanthanum, neodymium, praseodymium, samarium, gadolinium, and ytterbium[129].

More complicated compounds have also been recommended, such as cerium complexes[130], and Schiff bases with copper, cobalt, nickel, lead, cadmium, and tin ions[131]. The most effective is a stabiliser formed from the Schiff base *NN'*-bis-2-hydroxy-1-naphthylidene-ethylenediamine with copper ions, which increases the stability to thermal oxidation ninefold.

Compounds of ferrocene—acetylferrocene, 1,1'-diacetylferrocene[132], 1,1'-bisdimethylethoxysilylferrocene, and 1,3-bis-(1,1'-ferrocenylene)tetradimethylsiloxane—have been suggested as stabilisers[133].

Good results are obtained by using as stabilising additives dialkyl sebacates[134] and also dialkyltin oxide[135,136]. A stabilising effect has been noted with the acetylacetonates of chromium, zinc, magnesium, nickel, and cobalt[137], and also with trihexyloxyiron and tributoxyzirconium[138]. The authors showed that the improvement in stability of polydimethylsiloxanes produced by adding the above compounds was due to the formation, in the process of thermal degradation, of a new polymer having heteroatoms in the chain[139].

There are also references to the stabilisation of siloxane oils by treating them at 100–200°C with compounds capable of forming monofunctional trialkylsilyl groups in the presence of cation-exchange polymers of natural type[140].

Gruber, Klebanskii, et al.[141] recommend improving thermal stability by introducing compounds capable of acting as centres of orientation and thereby creating an ordered secondary structure. Among such recommended additives are oxides, both similar in nature to and different from the siloxane chain, as well as certain finely divided metals and oxides.

Although quite a wide range of stabilisers have already been proposed for polyorganosiloxanes, the problem of their stabilisation still remains a complicated task. The most effective would obviously be stabilisers combining the properties of an antioxidant with the ability to increase the stability of the main siloxane chain. Since polyorganosiloxanes are thermostable polymers, their thermal stability can probably be improved also by using thermally stable, non-volatile compounds which develop a stabilising action at high temperatures.

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Institute of Organoelementary Compounds, USSR Academy of Sciences, Moscow

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The Radical Addition and Telomerisation of Conjugated Dienes

I.B.Afanas'ev and G.I.Samokhvalov

Reactions are reviewed involving the radical addition and telomerisation of conjugated dienes with halogeno-derivatives of aliphatic hydrocarbons, thiols, sulphonyl chlorides, stannanes, t-butyl hypochlorite, chlorine, and hydrogen bromide. The mechanisms are examined of reactions occurring under the influence of the usual radical-generating initiators, and also of redox systems based on salts of metals of variable valency, peculiarities of the reaction of the growing chain in the allyl radical caused by its low reactivity. A considerable part of the paper deals with problems of the structural and steric isomerism of the addition products, the kinetics of the reactions under consideration, and the reactions of several analogues of conjugated dienes. A list of 86 references is included.

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I. INTRODUCTION

An unsaturated isoprenoid chain with regularly arranged methyl groups constitutes the basis of the structure of very important naturally occurring compounds, such as the carotenoids, vitamin A, the terpenes, natural rubber, side-chains of ubiquinones, and vitamins K and E. Its cyclisation yields cyclic mono-, di-, and tri-terpenes, and also their structural analogues, on which the structure of the steroid hormones, steroidal alkaloids, and several other natural compounds is based.

Considerable progress has been made during recent years in studying the biogenesis of natural isoprenoids, in identifying the intermediate compounds which form building blocks in their biosynthesis. However, much still remains obscure in understanding the processes of formation of unsaturated isoprenoid chains with their rigorous steric and structural specificity[1].

The reactions of the radical addition and telomerisation of conjugated dienes, leading to isoprenoids or their close analogues, have several specific features. The low activity and hence great selectivity of the growing allyl radical, the structural and steric isomerism of the telomers are of interest for the theory of free-radical reactions. Furthermore, investigations on the free-radical isomerisation and cyclisation of unsaturated compounds, in particular telomers of conjugated dienes, may open up a route to the synthesis of cyclic analogues of natural compounds.

The present review may be of interest to research workers concerned with the chemistry of free-radicals and to those dealing with the synthesis of natural compounds.

II. MECHANISM OF RADICAL REACTIONS OF CONJUGATED DIENES

In 1936 Kharasch et al.[2] discovered that peroxides influence the relative proportions of the isomeric bromobutenes formed by the reaction of buta-1,3-diene with hydrogen bromide. They therefore suggested a free-radical mechanism for the formation of the 1,4-isomer, which has since been confirmed many times. In the case of radical reactions of conjugated dienes the Kharasch mechanism can be represented by the general scheme

$$AX + R_i\cdot \rightarrow A\cdot + R_iX \quad \text{initiation} \qquad (1)$$

or

$$AX \xrightarrow{h\nu} A\cdot + X\cdot$$

$$A\cdot + \text{Diene} \rightarrow A(\text{Tel})\cdot \qquad (2a)$$

$$A(\text{Tel})\cdot + (n-1)\,\text{Diene} \rightarrow A(\text{Tel})_n\cdot \quad \text{chain growth} \qquad (2b)$$

$$A(\text{Tel})_n\cdot + AX \rightarrow A(\text{Tel})_nX + A\cdot \quad \text{chain transfer} \qquad (3)$$

$$2A\cdot \rightarrow \text{Products}$$

$$A(\text{Tel})_n\cdot + A(\text{Tel})_m\cdot \rightarrow \text{Products} \quad \text{chain termination} \qquad (4)$$

Here R_i is an initiator radical, AX a molecule of the compound (telogen) which adds to the diene. Addition of more than one diene molecule to the telogen radical A· leads to formation of a telomeric radical $A(Tel)_n$· and then to telomeric products $A(Tel)_nX$.

A fundamental difference between this mechanism and the mechanism of radical telomerisation of alkenes and unconjugated dienes is that in the present case the telomeric radical is allyl, which is relatively unreactive. Therefore the dissociation energy of the A–X bond and the

heat of reaction of the chain transfer (3) play a decisive part in effecting a chain mechanism. If the dissociation energy $D(A-X)$ is relatively high, and the heat of reaction ΔH of stage (3) negative, reaction becomes impossible (at ordinary temperatures) owing to the low activity of the radical $A(Tel)_n^{\cdot}$.

Table 1 gives tentative values of $D(A-X)$ and ΔH for the reactions of dienes $CH_2:CRCH:CH_2$ ($R = H$, CH_3) with several halogenated compounds. Since in this case addition should take place mainly at the 1,4-positions (Table 2), it was assumed in the calculations that

$$D\,(ACH_2CR{=}CHCH_2{-}X) \approx D\,(CH_2{=}CHCH_2{-}X).$$

In conformity with these calculations, investigation of the reactions of isoprene with the compounds listed in Table 1 has shown[4] that, in the presence of benzoyl peroxide or azoisobutyronitrile in glass ampoules, or also on ultraviolet irradiation at 20–100°C, only bromotrichloromethane reacts, the chain-transfer stage being least endothermic (almost thermoneutral) for this compound.

Table 1. Energy of dissociation of bonds $D(A-X)$ and heat of reaction of chain transfer ΔH for the addition of halogenated alkanes to conjugated dienes.

A–X	D(A–X)(Ref.3), kcal mole^{-1}	$D(ACH_2CR:CHCH_2-X)$ (Ref.3), kcal mole^{-1}	ΔH, kcal mole^{-1}
CCl_3—Br	49,5±3	47,5±2	−2±3
CCl_3—Cl	67	60,4±3	−7±3
C_2H_5—I	51	34,1±1,5	−17±1,5
CCl_3—H	90±3	77	13±2

An important variation of the Kharasch mechanism is the scheme of radical telomerisation of dienes initiated by redox systems based on salts of metals of variable valency. In this case the metal salts are involved in the stages not only of initiation but also of chain transfer. For example, carbon tetrachloride reacts readily with buta-1,3-diene[5,6] and isoprene[4] if the iron(III) chloride–diethylamine hydrochloride-benzoin system is used as initiator. It is supposed[6] that initiation and chain transfer take place by means of the following reactions (with butadiene):

$$FeCl_2 + CCl_4 \rightleftarrows FeCl_3 + CCl_3\cdot \qquad (5)$$

$$CCl_3(C_4H_6)_n\cdot + FeCl_3 \rightleftarrows CCl_3(C_4H_6)_nCl + FeCl_2\,. \qquad (6)$$

Both reactions are probably reversible. Since $D(FeCl_2{-}Cl) = 50$ kcal mole^{-1},[3] the heat of reaction (6) is $\Delta H \simeq +10$ kcal mole^{-1}: i.e. iron(III) chloride is a considerably more effective chain carrier than is carbon tetrachloride.

Another possible explanation of the action of redox systems is that the solvents used for homogenising the reaction mixture with redox initiation probably also take part in the reaction. Very reactive intermediate compounds ("mediators") can then be formed, which are efficient chain carriers. This mechanism was suggested[7] for the initiation by iron salts of the telomerisation of ethylene with carbon tetrachloride in propan-2-ol, it being assumed that the mediator is the chlorocarbinol $(CH_3)_2CCl(OH)$.

III. REACTIONS INVOLVING FISSION OF C–X BONDS (X = H, Hal) IN THE TELOGEN MOLECULE

In contrast to unconjugated dienes and alkenes, conjugated dienes react with great difficulty by a free-radical mechanism with compounds where chain transfer involves the C–X bond (X = H, Hal). This is explained by the relatively high dissociation energies of the bonds and the low activity of the telomeric allyl radical. The most detailed study has been made of the reactions of bromotrichloromethane, which reacts readily with buta-1,3-diene[8–12,14], isoprene[4,13], 2,3-dimethylbuta-1,3-diene[13], 2-t-butylbuta-1,3-diene[15,16], 1,1,3-trifluorobuta-1,3-diene[17], cyclopentadiene[18], and cyclohexa-1,3-diene[18]. Peroxides and exposure to visible light, ultraviolet radiation, X-rays, and γ-rays have been used to initiate these reactions. Thermal initiation is also possible. The main reaction product was the telomer $CCl_3(Tel)Br$ (n_1) with a chain length $n = 1$. In several cases products of high molecular weight were formed[9,11–13], the content of these compounds increasing with the duration of the reaction. This suggests that the telomer n_1 reacts in stages:

$$CCl_3(Tel)\,Br + CCl_3\cdot \rightarrow CCl_3Br + CCl_3(Tel)\cdot \qquad (7)$$

$$CCl_3(Tel)\cdot + Diene \rightarrow CCl_3(Tel)_2\cdot \xrightarrow{CCl_3Br} CCl_3(Tel)_2Br + CCl_3\cdot \qquad (8)$$

not in conformity with Eqn. (2b).

Isoprene reacts similarly with carbon tetrabromide (under the influence of γ-rays[19]), and butadiene with ethyl tribromoacetate (on ultraviolet irradiation[20]), with pentadecafluoro-1-iodoheptane (in the presence of azoisobutyronitrile[21] and on heating[22]), and with carbon tetrabromide (in the presence of potassium peroxodisulphate[23]). The addition of trichloroiodomethane to perfluorobutadiene under the influence of ultraviolet radiation has been described in the patent literature[24,25]. The reactivity of these telogens is close to that of bromotrichloromethane.

Telomerisation of carbon tetrachloride with buta-1,3-diene[26,27] and piperylene[27] in the presence of benzoyl peroxide, and that of chloroform with butadiene[29] in the presence of acetyl peroxide, have also been reported. The reactions with carbon tetrachloride were conducted only in steel autoclaves[26]. As mentioned in Section II, the allyl radical is unable to react at ordinary temperature with the C–Cl bond in carbon tetrachloride. The above results[26,27] therefore, are probably explained by the presence in the steel autoclaves of catalytic quantities of iron salts, which form redox initiator systems.

In the reaction of butadiene with chloroform[28] a large amount of initiator was used (molar ratio of acetyl peroxide to butadiene 1 : 2). The authors state that only the telomer n_2 was obtained, isomeric composition (45% 1,4-1,4-, 45% 1,2-1,2-, and 10% 1,4-1,2-isomers) being inconsistent with a radical reaction mechanism. Perhaps a side-reaction involving acetyl peroxide took place in this case.

An American patent[29] has described the reaction between chloroform and perfluorobutadiene in the presence of trichloroacetyl peroxide, but the structure of the reaction products was not determined.

The use of redox systems based on salts of metals of variable valency has recently enabled addition and telomerisation reactions to be accomplished between conjugated dienes and unreactive telogens. It has already been mentioned that carbon tetrachloride reacts with buta-1,3-diene[5,6] and isoprene[4] at 100–140°C under the influence of redox systems based on iron and copper salts. In the reaction with butadiene the telomer n_2 was isolated[6] as

Table 2. Content of isomers in products of addition (n_1) to conjugated dienes.

Telogen	R^a	Reaction temp., °C	Initiator	Telogen radical	Content of isomers in n_1, %			Ref.
					1,4-	4,1-	1,2-	
1	2	3	4	5	6	7	8	9
1. Reactions with butadiene $CH_2^1=CH^2CH^3=CH_2^4$								
CCl_3Br	4	50—60	uv[b]	$CCl_3\cdot$	75±10		25±10	8
CCl_3Br	1	20	X-rays	$CCl_3\cdot$	96.3 (*trans*)			12
$C_6H_5OCOCBr_3$	4	20	uv	$C_6H_5OCOCBr_2\cdot$	≈100 (*trans*)			20
$(CH_3)_2SnH_2$	1	25—50	uv	$(CH_3)_2HSn\cdot$	≈100 (*trans*)			39
$(C_2H_5)_2SnH$	0.5	40—70	ABN[c]	$(C_2H_5)_2Sn\cdot$	78±80 (*trans*)		20—22	41
(iso-$C_4H_9)_2SnHCl$	0.5	40—70	ABN	(iso-$C_4H_9)_2ClSn\cdot$	80—84 (*trans*)		16—20	41
$(C_4H_9)_2NCl$		—5—+15	d	$(C_4H_9)_2\overset{+}{N}H\cdot$	≈100 (*trans*)			45
CH_3SH	1	20	uv	$CH_3S\cdot$	96 (*trans*)		3	52
C_2H_5SH	1	20	uv	$C_2H_5S\cdot$	90 (*trans*)		4	52
C_2H_5SH	1	70	ABN	$C_2H_5S\cdot$	99 (80% *trans*, 20% *cis*)		1[e]	53
C_6H_5SH	1	20	uv	$C_6H_5S\cdot$	99 (*trans*)		1	52
CH_3COSH	1	20	uv	$CH_3COS\cdot$	98 (*trans*)		2	52
SF_3Cl	2.6	100	—				≈45	64,65
$(CH_3)_3COCl$		0	visible light	$(CH_3)_3CO\cdot$	74 (*trans*)		26	48
Cl_2		—9	uv	$Cl\cdot$	77[f] (*trans*)		23	69
HBr		—12	BP[g] ascaridole	$Br\cdot$	77±81		19—23[h]	2
$(C_5H_{11}COO)_2^i$ $Cu(OCOCH_3)_2$		26—50	—	$CH_3(CH_2)_4\cdot$	10—12 (*trans*)		88—90	70
$(CH_2=CHCH_2CH_2COO)_2$ $Cu(OCOCH_3)_2$		57	—	$CH_2=CHCH_2CH_2\cdot$	14 (*trans*)		86	70
=O, H_2O_2 CH_3OH, $CuSO_4$		0	—	$CH_3OOC(CH_2)_5\cdot$	23,2 (*trans*)		76,8	71
(cyclo-$C_6H_7COO)_2$ $Cu(OCOCH_3)_2$		26	—	(cyclo-$C_6H_7\cdot$	11 (*trans*)		89	70
$(CH_3)_2COOH$ $FeCl_3$, $CuCl_2$		0	—	$(CH_3)_2CO\cdot$	65 (*trans*)		35	48
$(CH_3)_3COOCOCH_3$ $Cu(OCOCH_3)_2$		0	—	$(CH_3)_3CO\cdot$	18—27 (*trans*)		73—82	48
CH_3COOK (electrolysis)		20	—	$CH_3\cdot$	≈78[k] (*trans*)		≈22	72
2. Reactions with isoprene $CH_2^1=C^2(CH_3)CH^3=CH_2^4$								
CCl_3Br	1.3	25—40	X-rays	$CCl_3\cdot$	71.9	26.1	0.5—1.5[l]	13
$(C_2H_5)_2SnH$	0.5	65—70	ABN	$(C_2H_5)_2Sn\cdot$		81—82(?)[m]		41
$(C_4H_9)_2SnHCl$	0.5	40—70	ABN	$(C_4H_9)_2SnCl\cdot$		67—68 (?)		41
(iso-$C_4H_9)_2SnHCl$	0.5	40—70	ABN	(iso-$C_4H_9)_2SnCl\cdot$		76—77(?)		41
CH_3SH	1	20	uv	$CH_3S\cdot$	76	22		52
C_2H_5SH	1	20	uv	$C_2H_5S\cdot$	75	25		52
C_6H_5SH	1	20	uv	$C_6H_5S\cdot$	97.5	2.5		52
CH_3COSH	1	20	uv	$CH_3COS\cdot$	89	10		52
=O, H_2O_2[i] CH_3OH, $CuSO_4$		0	—	$CH_3OOC(CH_2)_5\cdot$	17.5		82.5	71
$(CH_3)_2COOCOC_4H_5$ CuBr		60—70	—	$(CH_3)_2CO\cdot$	n			48
CH_3COOK (electrolysis)		20	—	$CH_3\cdot$	o			72
3. Reactions with *trans*-piperylene $CH_3^1=CH^2\diagdown CH^3=CH^4\diagdown CH_3$								
CH_3SH (75% conversion)	0.5	25	uv	$CH_3S\cdot$	49.5 (*trans*-) 4.4 (*cis*)	17.1	27.1 (*trans*-) 1.9 (*cis*)	60
CH_3SH (90% conversion)	0.5	25	uv	$CH_3S\cdot$	48.8 (*trans*-) 4.9 (*cis*)	14.6	29.3 (*trans*-) 2.4 (*cis*)	60
C_6H_5SH	0.5	25	uv	$C_6H_5S\cdot$	36.9 (*trans*-) 3.4 (*cis*)	6.2	51.4 (*trans*-) 2.1 (*cis*)	60

Table 2 (cont'd).

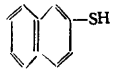
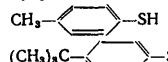
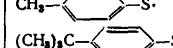
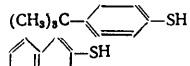
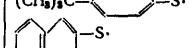
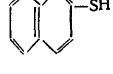
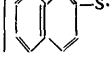
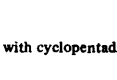
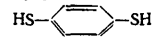
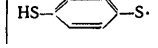
Telogen	k^a	Reaction temp., °C	Initiator	Telogen radical	Content of isomers in n_1, %			Ref.
					1,4-	4,1-	1,2	
1	2	3	4	5	6	7	8	9
4. Reactions with *cis*-piperylene $CH_2^1=CH\overset{3}{\underset{}{}}CH=CH\overset{4}{\underset{}{}}CH_3$								
CH_3SH (81% conversion)	0.5	25	uv	$CH_3S\cdot$	58.4 (*trans*-) 1.6 (*cis*)	21,1	5.9 (*trans*-) 13.0 (*cis*)	0
CH_3SH (96% conversion)	0.5	25	uv	$CH_3S\cdot$	47.8 (*trans*-) 3.2 (*cis*)	21,6	13.4 (*trans*-) 14.0 (*cis*)	60
C_6H_5SH	0.5	25	uv	$C_6H_5S\cdot$	56.8 (*trans*-) 0.0 (*cis*)	4,3	3.2 (*trans*-) 29.5 (*cis*)	60
$(C_2H_5)_3SnH$[p]	0.5	40—70	ABN	$(C_2H_5)_3Sn\cdot$	60—66		34—40	41
(cyclo-$C_6H_{11})_3SnH$	0.5	40—70	ABN	(cyclo-$C_6H_{11})_3Sn\cdot$	53—55		45—47	41
$(C_6H_5)_3SnH$	0.5	40—70	ABN	$(C_6H_5)_3Sn\cdot$	40—45		55—60	41
$(C_4H_9)_2SnHCl$	0.5	40—70	ABN	$(C_4H_9)_2SnCl\cdot$	55—57		43—45	41
(iso-$C_4H_9)_2SnHCl$	0.5	40—70	ABN	(iso-$C_4H_9)_2SnCl\cdot$	56—57		43—44	41
5. Reactions with 2,3-dimethylbuta-1,3-diene $CH_2^1=C(CH_3)^2C(CH_3)^3=CH_2^4$								
CCl_3Br	1	25—40	X-Rays	$CCl_3\cdot$	≈100			13
$(C_2H_5)_3SnH$	0.5	40—70	ABN	$(C_2H_5)_3Sn\cdot$	66—70		30—34	41
$(C_4H_9)_3SnH$	0.5	40—70	ABN	$(C_4H_9)_3Sn\cdot$	68—72		28—32	41
(iso-$C_4H_9)_3SnH$	0.5	40—70	ABN	(iso-$C_4H_9)_3Sn\cdot$	81—83		17—19	41
(cyclo-$C_6H_{11})_3SnH$	0.5	40—70	ABN	(cyclo-$C_6H_{11})_3Sn\cdot$	68—70		30—32	41
$(C_6H_5)_3SnH$	0.5	40—70	ABN	$(C_6H_5)_3Sn\cdot$	>90		<10	41
$(C_4H_9)_2SnHCl$	0.5	40—70	ABN	$(C_4H_9)_2SnCl\cdot$	62—63		37—38	41
(iso-$C_4H_9)_2SnHCl$	0.5	40—70	ABN	(iso-$C_4H_9)_2SnCl\cdot$	72—73		27—28	41
$(C_4H_9)_2SnH_2$	0.5	40—70	ABN	$(C_4H_9)_2SnH\cdot$	69—71		29—31	41
CH_3SH	1	20	uv	$CH_3S\cdot$	97		2.5	52
C_2H_5SH	1	20	uv	$C_2H_5S\cdot$	96		3	52
C_6H_5SH	1	20	uv	$C_6H_5S\cdot$	98		1	25
CH_3COSH	1	20	—	$CH_3COS\cdot$	99		1	52
	1	20	—		99			52
6. Reactions with 2,4-dimethylhexa-2,4-diene $(CH_3)_2C^1=C^2H\,C^3H=C^4(CH_3)_2$								
CH_3SH	1	20	uv	$CH_3S\cdot$	25 (*trans*-)		75	61
C_2H_5SH	1	20	uv	$C_2H_5S\cdot$	32 (*trans*-)		68	61
C_6H_5SH	1	95	—	$C_6H_5S\cdot$	24 (*trans*-)		76	61
	1	95	—		16 (*trans*-)		84	61
	1	95	—		15 (*trans*-)		85	61
	1	95	—		8 (*trans*-)		92	61
7. Reactions with 2-t-butylbuta-1,3-diene $CH_2^1=C^2(C(CH_3)_3)-C^3H=C^4H_2$								
CCl_3Br	2	56	visible light	$CCl_3\cdot$	50	50		16
C_6H_5SH	2	56	ditto	$C_6H_5S\cdot$	≈100			16
8. Reactions with 2-chlorobuta-1,3-diene $CH_2^1=CCl^2CH^3=CH_2^4$								
CH_3SH	1	20	uv	$CH_3S\cdot$	75	25		52
C_2H_5SH	1	20	uv	$C_2H_5S\cdot$	72	28		52
C_6H_5SH	1	20	uv	$C_6H_5S\cdot$	95	5		52
CH_3COSH	1	20	uv	$CH_3COS\cdot$	86	13		52
9. Reactions with 1,1,2-trifluorobuta-1,3-diene $CF_2^1=CF^2CH^3=CH_2^4$								
CCl_3Br	5	20	visible light	$CCl_3\cdot$	≈100			17
10. Reactions with cyclopentadiene 								
$(C_2H_5)_3SnH$	0.5	40—70	ABN	$(C_2H_5)_3Sn\cdot$	84—89		11—16	41
$(C_6H_5)_3SnH$	0.5	40—70	ABN	$(C_6H_5)_3Sn\cdot$	>90		<10	41
$(C_4H_9)_2SnHCl$	0.5	40—70	ABN	$(C_4H_9)_2SnCl\cdot$	94—96		4—6	41
(iso-$C_4H_9)_2SnHCl$	0.5	40—70	ABN	(iso-$C_4H_9)_2SnCl\cdot$	93—95		5—7	41
C_6H_5SH	1	20	—	$C_6H_5S\cdot$	58		42	41
	1	20	—		56		44	41

Table 2 (cont'd).

Telogen	R^a	Reaction temp., °C	Initiator	Telogen radical	Content of isomers in n_1, %			Ref.
					1,4-	4,1-	1,2-	
1	2	3	4	5	6	7	8	9
11. Reactions with cyclohexa-1,3-diene								
$(C_6H_5)_3SnH$	0,5	40—70	ABN	$(C_6H_5)_3Sn\cdot$	39—42		58—61	41
C_6H_5SH	1	20	—	$C_6H_5S\cdot$	57		43	61
HS—⟨⟩—SH	1	20	—	HS—⟨⟩—S·	56		44	62
12. Reactions with cyclo-octa-1,3-diene								
C_6H_5SH	1	20	—	$C_6H_5\cdot$	85		15	62
HS—⟨⟩—SH	1	20	—	HS—⟨⟩—S·	83		17	62
13. Reactions with 1,2-dimethylenecyclohexane								
H_3C—⟨⟩—SH	1	70—100	—	H_3C—⟨⟩—S·	≈100			63
14. Reactions with 3-methylenecyclohexene								
H_3C—⟨⟩—SH	1	70—100	—	H_3C—⟨⟩—S·	≈100			63
15. Reactions with 2,3-dimethylenebicyclo[2,2,1]heptane								
HS—⟨⟩—SH	1	20	—	HS—⟨⟩—S·	98		2	63

[a] Initial telogen : diene molar ratio.
[b] uv = ultraviolet irradiation.
[c] ABN = azoisobutyronitrile.
[d] Reaction conducted in strongly acid medium (H_2SO_4).
[e] 2,1-Isomer, $CH_3CH(SC_2H_5)CH:CH_2$.
[f] 1.5% of the *cis*-1,4-isomer may be present.
[g] BP = benzoyl peroxide.
[h] 2,1-Isomer, $CH_3CHBrCH:CH_2$.
[i] Reaction of peroxides with dienes in the presence of iron and copper salts.
[k] Ratio of 1,4- and 1,2-isomers determined from quantity of *trans*-hex-3-ene and 3-methylpent-1-ene formed by recombination of $CH_3C_4H_6^{\cdot}$ and $CH_3^{\cdot}$ radicals.
[l] Unidentified isomers.
[m] In the opinion of the authors the reaction products contain only 4,1- and 4,3-isomers.
[n] 1,2- and 4,3-Isomers.
[o] In the opinion of the authors, the *cis*-1,4-isomer. (See Section VII for the unreliability with which the configuration of addition products to isoprene can be identified.)
[p] Reaction with a mixture of *cis*- and *trans*-piperylene.

well as n_1. Chloroform reacts under similar conditions with butadiene[5,30,31], with the formation mainly of 1,5,5-trichloropent-2-ene:

$$CHCl_3 + CH_2{=}CHCH{=}CH_2 \xrightarrow{(FeCl_2,CuCl_2)} CHCl_2CH_2CH{=}CHCH_2Cl \qquad (9)$$

i.e. chloroform reacts with cleavage of the C–Cl bond. This confirms that chain transfer involves the metal salt ("ligand" transfer) or "carrier"[7], since chain transfer involving chloroform is accompanied predominantly by cleavage of a C–H bond[32].

When solutions of iron(II) chloride in acetonitrile are used, buta-1,3-diene reacts at 90–120°C with mono-, di-, and tri-chloroacetonitrile, allyl chloride, and 1,3-dichloropropene, isoprene with dibromoacetonitrile, chloroprene with but-2-enyl chloride and dichloroacetonitrile, and 2,3-dimethylbuta-1,3-diene with dibromoacetonitrile and trichloroacetonitrile[33]. In all cases the main product of the reaction was the telomer n_1. The reactions were accompanied by cleavage of C–Cl and C–Br bonds in the telogen molecules.

IV. REACTIONS INVOLVING FISSION OF Si–X, Sn–X, N–X, P–X, O–X, S–X, Cl–X, and Br–X BONDS (X = H, Hal) IN THE TELOGEN MOLECULE

1. Compounds of Group IV Elements (other than Carbon)

Trichlorosilane reacts with buta-1,3-diene at 300°C to form 1-trichlorosilylbut-2-ene [34], but in the presence of azo-compounds at 65–115°C readily hydrolysable telomers having $n = 7–8$ are obtained [35]. Trichlorosilane probably reacts similarly with perfluorobutadiene [36]. According to Steele et al. [37] the dissociation energy of the $Cl_3Si–H$ bond is 93 ± 4 kcal mole^{-1}, so that the chain-transfer stage should be strongly endothermic ($\Delta H \simeq -16$ kcal mole^{-1}). It has already been pointed out (Section II) that, with such a value for the heat of reaction of the chain-transfer stage, the addition of organic compounds to conjugated dienes is not very probable. It must be borne in mind, however, that the dissociation energies of bonds in organoelementary compounds have not been determined too reliably (see below). The dissociation energy of the Sn–H bond in organotin hydrides is relatively small (~50 kcal mole^{-1}) [38], and therefore alkyl- and aryl-stannanes (dimethyl-, trimethyl-, triethyl-, tricyclohexyl-, dibutyl-, triphenyl-, and di-isobutyl-stannanes) add easily to buta-1,3-diene [39,41] isoprene [41], piperylene [40,41], 2,3-dimethylbuta-1,3-diene [41], cyclopentadiene [41], and cyclohexa-1,3-diene [41] on heating, on exposure to ultraviolet radiation, and in the presence of azoisobutyronitrile, e.g.

$$(C_2H_5)_3SnH + CH_2{=}CHCH{=}CH_2 \rightarrow (C_2H_5)_3SnC_4H_7. \quad (10)$$

2. Compounds of Group V Elements

It has been reported in the patent literature that the telomerisation of buta-1,3-diene with ammonia can take place under the influence of γ-rays [42]. Telomers of general formula $NH_2[C_4H_6]_nH$ are obtained, where $n = 6, 7$. Since the dissociation energy of the N–H bond in ammonia is 103 kcal mole^{-1}, [43] the heat of reaction of the chain transfer (3) is $\Delta H \simeq -26$ kcal mole^{-1}. Therefore a radical chain reaction mechanism is improbable in this case.

Nitrogen compounds containing reactive N–Hal bonds may be expected to react by a free-radical mechanism. In fact, nitryl chloride NO_2Cl [44] and dialkylchloramines [45] add readily to buta-1,3-diene with cleavage of the C–Cl bond. However, a radical mechanism has been suggested only for the reaction with dialkylchloramines, the radicals being assumed to react in the protonated form (radical-cations). The addition of aliphatic azo-compounds to conjugated dienes undoubtedly occurs by a radical mechanism [46]. For example, azoisobutyronitrile reacts with butadiene at 75°C to form telomers having $n_{av} = 2–5$:

$$NC(CH_3)_2C{-}N{=}N{-}C(CH_3)_2CN \rightarrow 2(CH_3)_2CCN + N_2 \quad (11)$$

$$2(CH_3)_2\dot{C}CN + nC_4H_6 \rightarrow NC(CH_3)_2C(C_4H_6)_nC(CH_3)_2CN. \quad (12)$$

The chain-transfer stage (3) is probably absent from this reaction, the telomers being formed by the recombination of growing radicals.

Only one example of the addition of phosphines to conjugated dienes is known: dibutylphosphine reacts with buta-1,3-diene in the presence of azoisobutyronitrile to form the telomers n_1 and n_2. [47]

3. Compounds of Group VI Elements

According to Kochi [48] t-butyl hypochlorite adds to buta-1,3-diene under the influence of ultraviolet radiation:

$$(CH_3)_3COCl + C_4H_6 \rightarrow (CH_3)_3COC_4H_6Cl. \quad (13)$$

This reaction is the sole example of a radical chain addition to conjugated dienes with rupture of the O–X bond in the chain-transfer stage†.

Besides bromotrichloromethane, thiols mostly take part in free-radical addition reactions of dienes. Published values of D(RS–H) are 88 at 75 kcal mole^{-1} for methanethiol and benzenethiol [43]. It can therefore be expected that only thiophenol will react relatively easily, since in this case the heat of reaction of stage (3) is $\Delta H = +2$ kcal mole^{-1}. However, aliphatic thiols, for which $\Delta H \simeq -(10–11)$ kcal mole^{-1}, react quite well with conjugated dienes. It seems to us that the difference in reactivity between thiols and derivatives of aliphatic hydrocarbons (carbon tetrachloride, chloroform, etc.) may be apparent, since the above values of D(S–H) are not very reliable, and according to Refs. 49 and 50, for example, $D(CH_3S–H) = 83.1$ kcal mole^{-1}. Therefore further discussion of the energetics of chain transfer in the reactions of thiols will be possible only after values for the dissociation energies of the bonds involved have been refined.

The reactions of aliphatic thiols, thiophenol, thioacetic acid, β-thionaphthol, etc. have been described with buta-1,3-diene [52–59], isoprene [52,58], piperylene [52,60], 2,3-dimethylbuta-1,3-diene [52], 2-t-butylbuta-1,3-diene [16], 2,5-dimethylhexa-2,4-diene [61], chloroprene [52], cyclopentadiene [62], cyclohexa-1,3-diene [62], cyclo-octa-1,3-diene [62], 2,3-dimethylenebicyclo[2,2,1]heptane [62], 1,2-dimethylenecyclohexane [63], and 3-methylenecyclohexene [63]. Although the formation of telomers of high molecular weight was observed in several cases, the main products of the reaction were adducts of chain length $n = 1$.

In the absence of an initiator, sulphur chloride pentafluoride readily adds to buta-1,3-diene at 100°C: [64,65]

$$SF_5Cl + CH_2{=}CHCH{=}CH_2 \rightarrow SF_5C_4H_6Cl. \quad (14)$$

Similarly, alkane- and arene-sulphonyl chlorides react with conjugated dienes with cleavage of the S–Cl bond. In these compounds, however, the dissociation energy of the bond is probably quite high, and addition occurs only in redox systems based on salts of metals of variable valency. In these reactions, therefore, a "ligand" chain-transfer mechanism involving the metal salt should be operative (Section III), e.g. [66]

$$CH_3SO_2Cl + Cu^{1+} \rightarrow CH_3SO_2\cdot + Cu^{2+}Cl \quad (15)$$

$$CH_3SO_2\cdot + CH_2{=}CHCH{=}CH_2 \rightarrow CH_3SO_2C_4H_6\cdot \quad (16a)$$

$$CH_3SO_2C_4H_6\cdot + Cu^{2+}Cl \rightarrow CH_3SO_2C_4H_6Cl + Cu^{1+}. \quad (16b)$$

With the use of solutions of copper(II) chloride in acetonitrile (with or without the addition of diethylamine hydrochloride) or in dichloromethane at 70–100°C, buta-1,3-diene and isoprene react with benzenesulphonyl, benzene-*m*-disulphonyl, *p*-chlorobenzenesulphonyl, and toluene-*p*-sulphonyl chlorides [66–68].

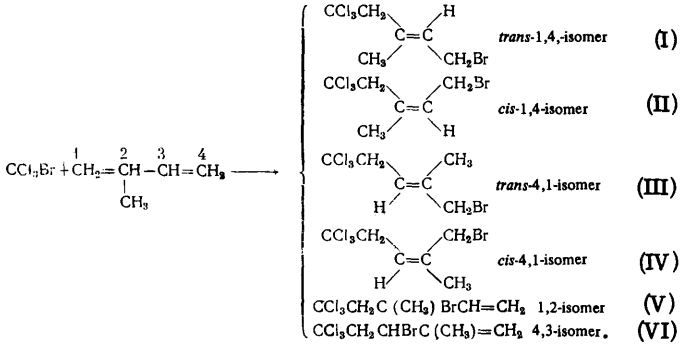
†The addition of peroxides ROOR and hydroperoxides ROOH [48,51] to dienes has a radical chain mechanism. However, instead of the chain transfer (3), the radicals here undergo oxidation by metal salts (Section V).

4. Compounds of Group VII Elements

Although the addition of halogens and hydrogen halides to conjugated dienes is well known, the free-radical character of the reaction has been demonstrated only in a few cases. As already mentioned (Section II), a radical mechanism was first suggested[2] actually for the reaction of hydrogen bromide with butadiene in the presence of peroxides. Even in this case, however, it is not possible to suppress ionic addition completely. In 1966 Poutsma showed[69] that the chlorination of buta-1,3-diene in the dark at −9°C in the absence of oxygen takes place mainly by a free-radical mechanism, although this reaction had previously been regarded as a classical example of electrophilic addition. The radical nature of the reaction was proved by the formation of chlorocyclohexane on the addition to the reaction mixture of cyclohexane, which does not undergo ionic chlorination. In the presence of oxygen—which inhibits the free-radical reaction—the quantity of chlorocyclohexane in the reaction products dropped sharply. On irradiation radical chlorination took place even in solvents. The reaction resulted in the adduct ClC_4H_6Cl, and the formation of higher telomers and tetrachloroalkanes was also noted. A free-radical mechanism is evidently possible also in the reactions of dienes with hydrogen chloride, bromine, and in other similar cases.

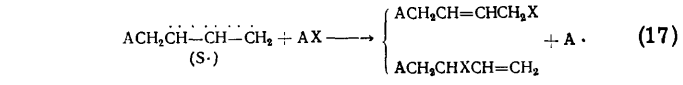
V. STRUCTURAL ISOMERISM OF TELOMERS. COMPETITION BETWEEN 1,2- AND 1,4-ADDITION

Even with the chain length $n = 1$ telomerisation products of conjugated dienes constitute a complicated mixture of both structural isomers and stereoisomers. As example a scheme is given below for formation of the n_1 telomer from bromotrichloromethane and isoprene (an unsymmetrical diene):



The possible reaction products are not exhausted by the six compounds given above, but the remaining compounds (2,1- and 3,4-isomers) are hardly formed at all, since free radicals attack mainly the terminal carbon atoms of the diene molecule. In the case of symmetrical dienes (buta-1,3-diene, 2,3-dimethylbuta-1,3-diene, etc.) the number of isomers diminishes to three (I, II, and V).

From the scheme for the chain-transfer reaction



which is mainly responsible for the ratio of 1,4- and 1,2-isomers (I and V) produced, it is seen that the relative quantities of these isomers should be determined by the dual reactivity of the allyl radical (S·), and hence should depend on the structure of the diene and the telogen. This radical S· exists predominantly in the form of the secondary radical, which is further stabilised by hyperconjugation of the unpaired electron with the ACH_2 group.

The relative proportions of 1,4- and 1,2-isomers found experimentally are given in Table 2. (It should be noted that reliable quantitative determination of the ratio (I) : (V), and also of other stereoisomers and structural isomers, has become possible only during recent years as a consequence of the development of methods of high-efficiency gas–liquid chromatography and nuclear magnetic resonance spectroscopy. Therefore papers and patents[5,6,10,11,21,22,26,33] which noted the formation only of 1,4-isomers—without the requisite careful analysis—require further checking, and are not included in Table 2.) It is seen from Table 2 that, even in the reactions of the same diene (e.g. buta-1,3-diene, which has been studied in greatest detail), the ratio (I) : (V) varies within wide limits (from ~ 100 : 0 to 10 : 90) depending on the nature of the telogen. This ratio is evidently determined mainly by the rate of reaction (17). The greater the rate of this reaction (i.e. the weaker the A–X bond which is cleaved and the greater the heat of reaction of chain transfer), the more probable is reaction of the more stabilised and consequently less active secondary radical S·, and hence the larger the amount of the 1,2-isomer formed. Thus among the products of reactions for which $\Delta H_{17} \leqslant 0$ (bromotrichloromethane, ethyl tribromoacetate, thiols, dialkylchloramines) the content of the 1,4-isomer is close to 100%, whereas when $\Delta H > 0$ (alkylstannanes, chlorine, and probably t-butyl hypochlorite) it is 75–80%.

Chain transfer is probably accomplished with still greater ease in the catalytic addition of peroxides[48,70]. In these reactions transfer of an electron by scheme (6) i.e. the redox reaction between the free radical and an ion of the metal of variable valency, takes place instead of the "ligand" chain transfer. For example, the following mechanism has been suggested[48] for the addition of acetyl t-butyl peroxide to buta-1, 3-diene in the presence of copper acetate:

$$(CH_3)_3COOCOCH_3 + Cu^{1+} \rightarrow (CH_3)_3CO\cdot + Cu^{2+}OCOCH_3 \quad (18)$$

$$(CH_3)_3CO\cdot + C_4H_6 \rightarrow (CH_3)_3COC_4H_6\cdot \quad (19)$$

$$(CH_3)_3COC_4H_6\cdot + Cu^{2+}OCOCH_3 \rightarrow (CH_3)_3COC_4H_6OCOCH_3 + Cu^{1+}. \quad (20)$$

Although the heat of reaction (20) is unknown, it is probably quite high, since the content of the 1,4-isomer falls to 10–30% (Table 2). "Ligand" chain transfer involving metal salts probably occurs at a lower rate, and therefore, in the addition of t-butyl hydroperoxide to butadiene in the presence of iron and copper halides, the content of the 1,4-isomer in the mixture of reaction products is 65%.[48]

The addition of the electrochemically generated methyl radical to buta-1,3-diene has been reported[72]. The ratio of 1,4- and 1,2-isomers is then 78 : 22, but in this case the ratio may be determined to a considerable extent by adsorption of radicals on the electrode.

The above reactions were conducted at temperatures between −10° and +100°C. Available data do not enable the dependence of the ratio of 1,4- and 1,2-isomers on the reaction temperature to be assessed, although rise in temperature must be expected to increase the content of the 1,2-isomer, which is formed by reaction of the less active secondary radical.

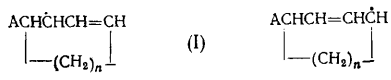
The structure of the diene also can influence the ratio of 1,4- and 1,2-isomers. Addition to isoprene produces an isomeric ratio (1,4 + 4,1) : 1, 2 which is close to the

corresponding ratio with butadiene (Table 2). In the reactions of *cis*- and *trans*-piperylene, both 1,2- and 1,4-isomers are formed from secondary radicals $ACH_2\dot{C}HCH:CHCH_3$ and $ACH_2CH:C\dot{C}HCH_3$, and therefore products of the reactions of thiols and stannanes with both isomeric piperylenes contain increased amounts of the 1,2-isomers in comparison with the reaction products obtained with buta-1,3-diene[60]. Moreover, the 4,1-isomer is formed, but the 4,3-isomer is absent. This result was to be expected, since the former isomer is produced from a primary radical, and the latter from a secondary radical. The ratio of 1,2- and 1,4-isomers in the reaction products of bromotrichloromethane, stannanes, and thiols with 2,3-dimethylbuta-1,3-diene[13,41,52] and with buta-1,3-diene changes little on passing from one diene to the other.

In the reactions of 2,5-dimethylhexa-2,4-diene[61], however, the 1,2-isomer becomes the main product (68–92% of the total composition of the telomer n_1), since formation of the 1,4-isomer involves the still less active tertiary radical $AC(CH_3)_2CH:C\dot{C}(CH_3)_2$.

1,2-Isomers are absent among products of the addition of bromotrichloromethane and butanethiol to 2-t-butylbuta-1,3-diene[16].

The addition of a telogen radical to cyclic conjugated dienes yields only secondary radicals (I) and (II)



(I)

(II)

so that in these cases formation of 1,4- and 1,2-isomers should be about equally probable. The quantities of 1,4- and 1,2-isomers found experimentally vary respectively within the limits 40–90% and 10–60% (Table 2). The reaction products obtained from conjugated methylenecycloalkenes (3-methylenecyclohexene, 1,2-dimethylenecyclohexane, 2,3-dimethylenebicyclo[2,2,1]heptane[63]) comprise almost entirely 1,4-isomers, since the radicals leading to 1,2-isomers are tertiary.

VI. STRUCTURAL ISOMERISM OF TELOMERS. COMPETITION BETWEEN 1,4- AND 4,1-ADDITION

Structural 1,4–4,1-isomerism is possible for the products of addition to unsymmetrical dienes, the relative content of the two isomers depending on the nature and position of the substituent in the diene molecule. If the substituent is attached to a quaternary carbon atom, the radical from which the 1,4-isomer is formed is secondary, i.e. more stable. Furthermore, in this case steric hindrance to attack by the free radical on the substituted end of the diene molecule is possible. Both effects tend to prevent formation of 4,1-isomers, and therefore the content of 1,4-isomers in the products from *cis*- and *trans*-piperylenes with thiols[60] exceeds by factors of 3–10 the content of the 4,1-isomers.

The influence of substituents in position 2 of a conjugated diene on the distribution of 1,4- and 4,1-isomers is more complicated. Both radicals ($ACH_2CY:CHCH_2^{\cdot}$ and $ACH_2CH:CYCH_2^{\cdot}$) responsible for formation of the corresponding isomers are primary, and their reactivity can be differentiated only by means of an indirect (polar, resonance, or steric) effect of the substituent Y. Results obtained for additions to isoprene show (Table 2) that the introduction of a methyl group into a diene molecule leads to the formation mainly of 1,4-isomers‡. The predominance of 1,4-isomers in this case is probably explained by greater stabilisation of the radical $ACH_2C(CH_3):CHCH_2^{\cdot}$ than of $ACH_2CH:C(CH_3)CH_2^{\cdot}$, by hyperconjugation of the unpaired electron with the methyl group. The polar effect of the methyl group can probably be neglected. This is seen from the example of the reactions of bromotrichloromethane and thiols with isoprene, 2-t-butylbuta-1,3-diene, and chloroprene: reaction of bromotrichloromethane with isoprene yields 71.9% of the 1,4-isomer and 26.1% of the 4,1-isomer[13], but in the reaction with 2-t-butylbuta-1,3-diene 50% of each isomer is formed[16]. Thus, although the polar effect of the t-butyl group exceeds that of the methyl group (the Taft constant $\sigma^*_{(CH_3)_3C} = -0.300$ [73]), the absence of α-hydrogen atoms makes the group almost incapable of hyperconjugation with the unpaired electron, so that it does not influence the distribution of 1,4- and 4,1-isomers resulting from attack by the trichloromethyl radical. On the other hand, the distribution of 1,4- and 4,1-isomers in the addition products of thiols to chloroprene[52] is the same as in reactions with isoprene[52], although such a strongly electronegative substituent as chlorine ($\sigma^*_{Cl} = 2.9$ [73]) should have more strongly prevented attack by the electrophilic radicals RS$^{\cdot}$ in position 1 than in position 4. The predominance of the 1,4-isomer in this case is probably explained by stabilisation of the corresponding radical by hyperconjugation with the chlorine atom.

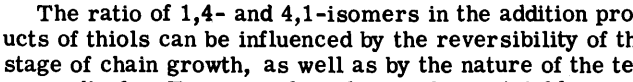
As already remarked, the ratio of 1,4- and 1,2-isomers is determined primarily by the molecular structure of the conjugated diene and the rate of chain transfer. However, 1,4—4,1-isomerism of addition products is probably influenced to a considerable extent also by the nature of the attacking free radical. A radical containing polar substituents will obviously add to the diene in such a way that unfavourable interactions with polar substituents of the diene will be minimised. In the reaction of bromotrichloromethane with 1,1,2-trifluorobuta-1,3-diene, for example, the trichloromethyl radical adds to the diene only at the fourth carbon atom, which then leads to formation of the 1,4-isomer $BrCF_2CF:CHCH_2CCl_3^{\cdot}$:

Stabilisation of a telogen radical increases its selectivity, so that the less active a free radical the greater the probability of formation of a more stabilised radical by reaction with a diene. It is therefore likely that the difference in reactivity between free radicals explains the diminished content of the 4,1-isomer in the reactions of isoprene with the radicals $CCl_3^{\cdot}$ [13] and $CH_3OOC[CH_2]_5^{\cdot}$ [71] respectively. The influence of the nature of the telogen radical can be traced most clearly in the reactions of isoprene with thiols as example. Reaction of isoprene with ethanethiol, as in the case of bromotrichloromethane, yields 75% of the 1,4-isomer and 25% of the 4,1-isomer[52]. In the reactions with thioacetic acid and thiophenol, however, the content of the 4,1-isomer falls to 10% and 2.5% respectively[52]. The reason for this change in the ratio of the isomers is evidently increased stabilisation and hence diminished reactivity of the free radicals in the sequence $C_2H_5S^{\cdot}$, $CH_3COS^{\cdot}$, $C_6H_5S^{\cdot}$. Thus determination of the relative rates of addition to the first and the last carbon atom of an

‡An exception is Neumann and Sommer's paper[41], in which it is stated, on the basis of an analysis of the infrared spectra, that predominantly 4,1-isomers are formed by the reaction of alkylstannanes with isoprene. In our opinion, however, this assertion, which contradicts the results of other investigations, requires further confirmation.

unsymmetrical diene can be used to estimate the resonance stabilisation of the added free radical.

The ratio of 1,4- and 4,1-isomers in the addition products of thiols can be influenced by the reversibility of the stage of chain growth, as well as by the nature of the telogen radical. For example, whereas bromotrichloromethane adds to 2-t-butylbuta-1,3-diene to form equal amounts of 1,4- and 4,1-isomers, only the former isomer is obtained with butanethiol[16]. The authors explain this anomaly by the reversibility of the addition of thiyl radicals to the diene:



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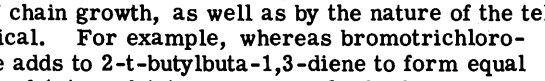
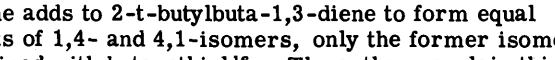


(22a)

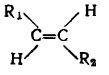


(22b)

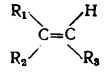
The probability of the formation of radicals (A) and (B) on the addition of $C_4H_9S^{\cdot}$ is the same as in the case of the trichloromethyl radical, but if, owing to steric hindrance due to screening of the reaction centre by the t-butyl group, the rate of chain transfer (22b) is considerably lower than the rate of reaction (21), the 4,1-isomer will be almost completely absent. It is interesting that, if the suggested mechanism is correct, the ratio of 1,4- and 4,1-isomers for analogous reactions should depend on the thiol : diene ratio, since the rate of reaction (22b) depends on the thiol concentration, whereas the rate of reaction (21) is independent thereof.

VII. STEREOISOMERISM OF TELOMERS

As already mentioned (Section V), stereoisomerism (*cis–trans*) is possible in the reaction products of 1,4- and 4,1-addition. In most of the work, unfortunately, the spatial configuration of the telomers has been determined only by infrared spectroscopy without separation of the isomers. Infrared spectra enable the presence only of a *trans*-isomer having two substituents adjacent to the double bond



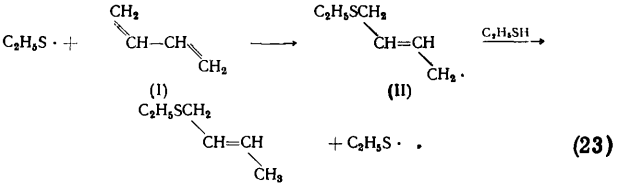
to be established reliably (frequency of deformation vibration of C–H bond 965 cm^{-1}), whereas the absorption frequency of the corresponding *cis*-isomer (728–675 cm^{-1}) is not characteristic[74]. Determination of the steric configuration of compounds containing three substituents adjacent to the double bond



is probably impossible from the infrared spectra, so that there are hardly any data on the *cis–trans*-isomerism of addition products to conjugated dienes containing substituents attached to the second carbon atom.

Most authors consider that radical 1,4-addition to buta-1,3-diene yields only the *trans*-isomer (Table 2). Although relatively small amounts of the *cis*-isomer might be formed and remain undetected for the reason indicated above, the predominant formation of the *trans*-isomer can evidently be accepted as proved. For example, Poutsma[69] showed by gas–liquid chromatography that the 1,4-isomer formed by reaction of chlorine with buta-1,3-diene was identical with the known *trans*-isomer, while the *cis*-isomer was absent from the mixture of reaction products. In contrast to the results obtained by most other authors, Jacobs and Illingworth[53] found that ethanethiol reacts with butadiene in the presence of azoisobutyronitrile at 70°C to form a mixture of addition products comprising 80% of the *trans*-isomer and 20% of the *cis*-isomer. However, the products of the same reaction under the influence of ultraviolet radiation at 20°C contain not more than 6% of the *cis*-isomer[52].

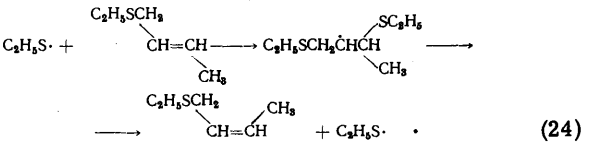
The configuration of telomers is evidently determined by the steric structure of the diene[60] and the possibility of isomerisation of the resulting addition product. At ordinary temperatures buta-1,3-diene occurs mainly (> 96%) in the more stable transoid conformation (I).[75] If, therefore, the initial conformation of the diene molecule is preserved during addition of the telogen radical and the subsequent chain-transfer reaction, the resulting telomer will have the *trans*-configuration:



(23)

With rise in temperature the content of butadiene in the *cis*-conformation increases, and the probability of change in the spatial conformation of the radical (II) also increases, which should lead to an increase in the yield of the *cis*-1,4-isomer. In fact, raising the temperature from 0° to 100°C in the radical polymerisation of butadiene leads to an increase in the *cis*-units in the polymer from 12% to 35%.[76]

Conducting the reaction at a low temperature and excluding the effect of metallic walls of the reaction vessel enable thermal and catalytic isomerisation of the products to be avoided. However, the presence of free thiyl radicals, as well as bromine and iodine atoms, in the reaction medium may cause isomerisation of the telomers as a consequence of the ability of these radicals to add reversibly at a double bond:



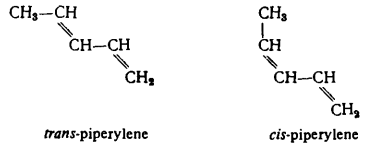
(24)

Therefore the increase in the yield of the *cis*-product of the addition of ethanethiol to butadiene with rise in reaction temperature from 20° [52] to 70°C [53] can be explained both by increase in the relative content of butadiene in the cisoid conformation and by isomerisation of the *trans*-isomer by thiyl radicals.

As in the case of buta-1,3-diene, the interaction of thiols with 2,5-dimethylhexa-2,4-diene[61] involves predominant formation of the *trans*-1,4-isomer compared with the *cis*-1,4-isomer.

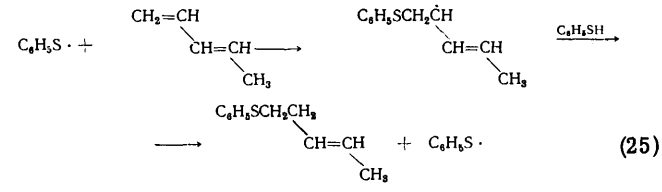
A detailed study has been made[60] of the stereoisomerism of addition products of thiols with *cis*- and *trans*-piperylene, when it was assumed that, as with buta-1,3-diene,

both isomers of piperylene exist in the more stable transoid conformation:



trans-piperylene *cis*-piperylene

Therefore the 1,4-isomers of the addition products, independently of the spatial structure of the initial diene, had the *trans*-configuration. Investigation of the isomerism of the 1,2-addition products enabled the dependence of the steric structure of the radical on the structure of the telogen (thiol) to be determined. It was found that 1,2-isomers of the reaction products with thiophenol were formed from radicals which preserved the configuration of the diene: i.e. *trans*-piperylene yielded mainly the *trans*-1,2-isomer, whereas *cis*-piperylene gave the *cis*-1,2-isomer:



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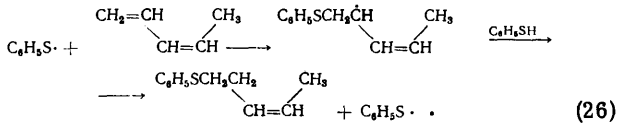


(26)

When thiophenol was replaced by aliphatic thiols, the stereospecificity of 1,2-addition dropped sharply. Thus the reaction of *cis*-piperylene with methanethiol (at 96% conversion of the latter) led to the formation of 14% of *cis*- and 13.4% of *trans*-1,2-isomers. The loss of stereospecificity is explained by a decrease in the rate of chain transfer via methanethiol molecules (in comparison with benzenethiol), and hence an increase in the lifetime of the free allyl radical, this in turn increasing the probability of change in its steric configuration.

The principal factors influencing the relative proportions of structural isomers and stereoisomers in the mixture of reaction products from conjugated dienes can be summarised as—(1) the structure of the dienes, (2) the structure of the telogens, (3) stabilisation of the telomeric (allyl) radical, (4) the polar effect of the reaction, (5) the temperature of the reaction, (6) the relative rates of forward and reverse reactions in the addition of the telogen radical to the diene, and (7) isomerisation of the reaction products.

VIII. KINETIC INVESTIGATIONS

Few kinetic data are available on the free-radical addition and telomerisation of conjugated dienes. Investigations have been made of the kinetics of the radical addition of ethyl tribromoacetate to butadiene[20] and of bromotrichloromethane to butadiene, isoprene, and 2,3-dimethylbuta-1,3-diene[12,13]. It was found that the reaction velocity was independent of the diene concentration but increased with the concentration of the telogen. These data suggest that even at high telogen : diene ratios the rate-determining stage of the reaction is chain transfer. With a bromotrichloromethane : diene ratio of 3 the reaction velocity is approximately proportional to the square root of the rate of initiation, and in the case of ethyl tribromoacetate to the rate of initiation to the power 0.83. Thus with bromotrichloromethane chain termination is bimolecular, whereas with ethyl tribromoacetate termination is possible also by a unimolecular mechanism. The overall activation energies for the reactions of bromotrichloromethane with butadiene, isoprene, and dimethylbutadiene are respectively 5.45, 3.96, and 3.09 kcal mole^{-1}.

Chain-transfer constants have been determined for the telomerisation of buta-1,3-diene with aliphatic thiols[77,78]. The values obtained (at 0–60°C) lie in the range from 3–6 (for tertiary thiols) to 15–25 (for primary thiols). Sivertz and his coworkers[79] used the rotating sector method to determine the chain-transfer rate constant for the telomerisation of isoprene with butanethiol (93 M^{-1} s^{-1} at 25°C).

Table 3. Ratio of rate constants for the addition of free radicals to butadiene and to ethylene.

Radical	Temp., °C	$\frac{k_{Bu}}{k_{Et}}$	Ref.
CH_3[b]	25	94	80
CH_3[b]	65	53	81
CH_3[c]	65	43	8
CCl_3[c]	50—60	18[a]	82
CF_3[c]	65	11.6	80

[a] Compared with the rate of addition to oct-1-ene.
[b] In the gas phase.
[c] In the liquid phase.

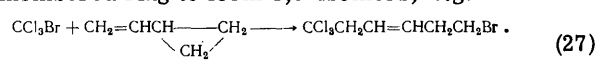
The addition of several free radicals to buta-1,3-diene in both gaseous and liquid phases has been investigated. Table 3 shows that the rate constants for addition of free radicals to butadiene are considerably higher than to ethylene, which is undoubtedly explained by resonance stabilisation of the allyl radical formed. Because of the high rate constants for addition of the radicals, the rate-determining stage in telomerisation and addition to conjugated dienes is chain transfer.

IX. ANALOGUES OF CONJUGATED DIENES

The free-radical additions of thiols to conjugated alkenynes—butenyne, 2-methylbutenyne, etc.—investigated by Sulimov and Petrov[83] are of considerable interest. These workers found that, of the six possible structural isomers in the reaction of thiols with butenyne, only four—e.g. (I) $CH_3SCH_2CH_2C:CH$ (39%), (II) $CH_3SCH_2CH:C:CH_2$ (40%), (III) $CH_2:C(SCH_3)CH:CH_2$ (18%), and (IV) $CH_3SCH::CHCH:CH_2$ (3%)—were formed. (The mixtures of isomers were analysed by gas–liquid chromatography and also by infrared and nuclear magnetic resonance spectroscopy.) The results show that thiyl radicals attack the butenyne molecule mainly at the double bond, the 1,2- and 1,4-isomers (I) and (II) being formed in roughly equal quantities. It is noteworthy that in this case the radical

$CH_3SCH_2CH:C:CH^{\bullet}$, from which the 1,4-isomer is formed, is not allylic, and is probably considerably less stabilised than is the secondary radical $CH_3SCH_2\dot{C}HC:CH$. The reactions of butenyne with benzenethiol, and of substituted butenynes with ethanethiol and butanethiol, yield only two isomers, corresponding to (I) and (II).

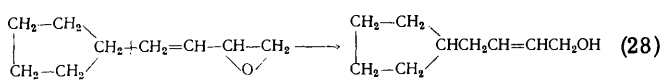
Compounds in which a double bond can be conjugated with a three-membered ring can also be regarded as analogues of conjugated dienes. Work has been done on the addition and telomerisation of vinylcyclopropane [84,86], isopropenylcyclopropane [85], and also their oxygen-containing derivatives [86] and butadiene monoxide [84] with bromotrichloromethane, carbon tetrachloride, thiols, propan-2-ol, and cycloalkanes in the presence of benzoyl peroxide and under the influence of radiation. Vinylcyclopropane and isopropenylcyclopropane reacted with cleavage of the three-membered ring to form 1,5-isomers, e.g.



$$CCl_3Br + CH_2{=}CH\text{–}\underset{\diagdown\,CH_2\,\diagup}{CH}\text{–}CH_2 \longrightarrow CCl_3CH_2CH{=}CHCH_2CH_2Br . \qquad (27)$$

An exception was provided by the reaction with thiols, which, depending on the structure of the vinylcyclopropane derivatives, produced, owing to their high reactivity, a mixture of rearranged and unrearranged (without ring cleavage) products or even one of the possible isomers [85,86].

A study of the three-dimensional structure of the reaction products of vinylcyclopropane with bromotrichloromethane showed [84] that the 1,5-isomer is an equilibrium mixture of *cis*- and *trans*-forms. The establishment of equilibrium was proved by the fact that additions of iodine and methanethiol do not affect the proportions of the stereoisomers. On the other hand, since 1,5-isomers formed from butadiene monoxide with cycloalkanes and isopropyl alcohol in conformity with the scheme



$$\begin{matrix} CH_2\text{–}CH_2 \\ | \qquad\quad \diagdown \\ CH_2\text{–}CH_2 \end{matrix} CH_2 + CH_2{=}CH\text{–}CH\text{–}CH_2 \longrightarrow \begin{matrix} CH_2\text{–}CH_2 \\ | \qquad\quad \diagdown \\ CH_2\text{–}CH_2 \end{matrix} CHCH_2CH{=}CHCH_2OH \qquad (28)$$

have the *trans*-structure, it was considered that the reaction of bromotrichloromethane with cyclopropane at first also yields exclusively (or predominantly), the *trans*-isomers, which only then are converted, under the influence of bromine atoms, into an equilibrium mixture of the two isomers. (Bromine atoms are formed from bromotrichloromethane at the stage of initiation by ultraviolet radiation.) In conformity with this, the telomers formed by the reaction of cyclohexane with vinylcyclopropane (in which no atoms or free radicals capable of reacting reversibly with a double bond are present) are probably *trans*-isomers [84].

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All-Union Scientific Research
Institute for Vitamins (VNIVI),
Moscow

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Electronic Factors in Catalytic Reactions Under the Influence of Ionising Radiation

G.M.Zhabrova and V.I.Vladimirova

A comprehensive analysis of published data on catalytic reactions under the influence of ionising radiations is given. The combination of heterogeneous catalysis and ionising radiation effects is shown to be a new area in which the study of electronic factors leads to an understanding of the role of free and of localised charge carriers in the elementary acts of catalytic reactions. Some problems in the electronic theory of catalysis involving the effect of radiation are formulated, and data on the role of the catalytically active centres produced by prior irradiation of the catalyst are reported. Catalytic reactions taking place under the influence of ionising radiation are discussed, and possible mechanisms (usually involving electronic and free-radical steps) are considered. 138 references.

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I. PROBLEMS IN THE ELECTRONIC THEORY OF CATALYSIS INVOLVING THE EFFECT OF RADIATION ON SOLIDS

The use of ionising radiation in the study of heterogeneous catalysis offers the possibility of controlled modification of the electronic properties of solid catalysts.

It is well established[1-5] that the main effect of ionising radiation on solids is to generate excess charge carriers (electrons and holes). In some cases structural defects are produced.

These effects, often accompanied by colour changes, enhanced electrical conductivity, and paramagnetic properties, are intimately connected with the catalytic activity of the solid. Therefore, the use of ionising radiation in the study of catalysis and catalytic reactions can provide additional information on the role of various defects and impurities, and also on the formation of catalytically active centres and on the effect of the concentration of excess current carriers on the catalytic properties of solids†.

Thus, the purpose of using an agency as powerful as radiation in heterogeneous catalysis is to generate structural defects able to act as catalytically active centres. From the standpoint of the electronic theory of catalysis the main interest lies in the appearance of excess charge carriers in solids exposed to irradiation, i.e. of electrons and holes, which can take part in the elementary acts of chemical reactions on catalyst surfaces.

Over 30 years ago the founder of the electronic theory of catalysis (Pisarzhevskii[6]) carried out the first investigations of the combined effect of radiation and catalysts on chemical reactions. He was able to show that the rate of oxidation of hydrogen on platinum is significantly increased by the action of u.v. radiation. The effect of u.v. and X-rays on hydrogen peroxide decomposition catalysts (platinum, graphite, lead dioxide) was more complicated: depending on the experimental conditions and on the pretreatment of the catalyst, the reaction could be accelerated or inhibited. Pisarzhevskii's explanation of this behaviour relies on the relative number of active centres, which can increase or decrease on different parts of the surface.

† This review is not concerned with photocatalytic and photoadsorption effects, which constitute a self-contained field of study.

We need not dwell on this early period of the study of radiation effects in catalysis: the development of radiation catalysis as a field of study began in the late 1950's, following the advances in nuclear technology and in solid-state physics and physical chemistry. Significant advances in the study of the electronic mechanism of catalytic reactions and of their elementary acts were also made at about this time[7-9].

The modern electronic theory of catalysis, based on the band model of the solid state, is primarily concerned with catalysts having semiconductor properties[9]. However, the conclusions of the electronic theory are equally applicable to dielectrics, because these two classes of solids differ only in the width of the forbidden gap. According to the electronic theory, the entities responsible for the adsorption and catalytic properties of solids are electrons and holes, which can be either free or localised on lattice defects. The equilibrium concentrations of these carriers are determined by the position of the Fermi level at the surface, itself a function of the bulk Fermi level. Various factors, known to influence the position of the Fermi level, can be expected to affect the adsorption and catalytic properties of the semiconductor.

Attempts are now being made to apply the electronic models of the theory of adsorption and catalysis to the effect of radiation on the catalytic and adsorption properties of semiconductors. Vol'kenshtein[10-13] treats radiation as a factor with a profound effect on the electronic structure of solids. Two limiting cases can be envisaged. In the first case the effect of radiation is confined to direct ionisation, i.e. to the generation of non-equilibrium concentrations of charge carriers in the semiconductor, and hence to a perturbation of the electronic equilibrium in the solid. The perturbation decays very rapidly when the source of radiation is removed. "Memory" effects, i.e. permanent changes in the catalytic and adsorption properties, are practically non-existent in semiconductors. A radiation-induced "memory", on the other hand, can persist for a long time in the second limiting case, when the preliminary irradiation (e.g., by neutrons) induces a nuclear reaction in the semiconductor and is therefore equivalent to chemical doping. There is also an intermediate, and very common, case in which irradiation produces structural defects without altering the chemical composition of the semiconductor.

The resulting radiation "disorder" of the lattice shifts the Fermi level and thus displaces the electronic equilibrium. On ceasing the irradiation electronic equilibrium in the semiconductor is gradually re-established. This process is accelerated by heating. Vol'kenshtein discusses also the case of an anomalous radiation-induced "memory", which can persist for relatively long periods after irradiation is discontinued even though no structural defects have been produced. The anomalous memory effect manifests itself as a change in the catalytic and adsorption properties of the catalyst, and is ascribed to trapping of the radiation-induced non-equilibrium current carriers on intrinsic surface defects (i.e. defects originating otherwise than by the action of radiation). Thus, the anomalous radiation-induced memory is closely associated with the concept of F, V, and other centres, which can be treated as electrons and holes trapped at cation and anion vacancies. The existence of these centres has been established by extensive investigations of the radiation physics of solids[1,4,5]. In the following section we shall discuss experimental evidence that centres of this type can be catalytically active in previously irradiated catalysts (mainly in insulators).

On the basis of the general ideas of the electronic theory, Vol'kenshtein[12,13] has discussed the mechanism by which previous irradiation can affect the kinetics and the equilibrium of adsorption processes, and the rate of catalytic reactions. He has shown, in particular, that for a given set of irradiation conditions the magnitude and the sign of the effect are determined by the temperature and by the initial value of the Fermi level.

Baru and Vol'kenshtein[14,15] have considered, from the standpoint of the electronic theory of chemisorption and catalysis, the mechanism of charge formation and of ionisation in a semiconductor subjected to radioactive self-irradiation (i.e. doped with a radioactive element). They were able to define the conditions under which one or the other of these competing mechanisms is predominant.

Coekelbergs and coworkers[16] gave a theoretical analysis of the effects stemming from a change in the steady-state concentration of charge carriers, and calculated the influence of this change on the kinetics and the equilibrium of heterogeneous catalytic reactions.

Thus, the use of ionising radiation has stimulated further developments in the electronic theory of catalysis. It must be stressed that existing theoretical ideas are as yet largely qualitative, because of the lack of key experimental data on the localised energy levels of various defects and impurities in the solid or arising from adsorbed molecules. There are no data on excess carrier concentrations, surface barrier heights, etc. after irradiation. Special investigations, and refined experimental techniques, are needed to obtain this type of information.

II. NATURE OF THE ACTIVE CENTRES FORMED BY PRIOR IRRADIATION OF THE CATALYST

The physical and chemical processes induced by prior irradiation give rise to "long-lived" active centres on the surface of the catalyst. Catalysts which have been thus modified by radiation can then be used in ordinary heterogeneous catalytic reactions.

The effect of prior irradiation on catalyst activity has been the object of extensive investigations: references to the early work can be found in existing review articles[17-22]. It should be noted that the formation of active centres is only one of the phenomena which can determine the influence of prior irradiation on the catalytic activity of the sample. Thus, there are reports of prior irradiation causing poisoning of the catalyst[23], desorption of catalytic poisons from the surface[24,25], and enhanced gas adsorption[26,27], which also affects the catalytic activity. Prior irradiation can also influence the topochemical stage of catalyst preparation, and thus affect its properties[28]. Hence, it is essential to exclude all these complicating factors when studying the effect of radiation on catalytic activity: in particular, the catalysts must be thoroughly degassed before irradiation to ensure reproducible results.

Since most catalytic reactions take place at elevated temperatures, the stability of the radiation-induced active centres becomes an important consideration. For the same reason, the model reactions chosen to investigate the effect of irradiation on catalytic activity are usually relatively simple, low-temperature reactions, such as hydrogen isotope exchange, hydrogen peroxide decomposition, ethylene hydrogenation, oxidation of carbon monoxide, etc. For convenience, we shall classify the published data by catalyst type (metals, semiconductors, and insulators).

With metallic catalysts, prior irradiation with gamma rays usually produces only a very small increase or decrease in the activity towards low-temperature reactions such as the decomposition of hydrogen peroxide[29,30], the oxidation of hydrogen on platinised alumina–silica[31], and the hydrogenation of nitrobenzene on nickel and platinum catalysts[32].

With high-temperature reactions (e.g. the dehydrogenation of cyclohexene on platinised alumina–silica[29] and the dehydrogenation of cyclohexane on a copper catalyst[33]), prior irradiation had no effect on the activity of the catalyst. More significant changes in activity were observed after bombarding metallic catalysts with inert gas ions[34,35] or neutrons[33].

Prior irradiation of catalysts of the semiconductor or insulator type can also produce either an increase or a decrease in catalytic activity, depending on the particular catalyst, on the irradiation conditions, and on the type of radiation, and also on the chosen reaction.

The radiation-catalytic effects of gamma radiation invariably show a fast decay (annealing) on raising the temperature. Thus, the catalytic activity of silica gel and alumina towards the hydrogen–deuterium isotope exchange reaction induced by gamma irradiation disappears even at 0°C.[36] Changes in catalytic activity produced by neutron irradiation are much more stable[24,36-39].

Small changes in catalytic activity after irradiation have been observed in the oxidation of carbon monoxide on cuprous oxide[40], nickel oxide, and zinc oxide[41], in the dehydrogenation of ethanol on copper oxides[42], in the oxidation of formic acid on a carbon catalyst[43], and in the decomposition of hydrogen peroxide on nickel oxide[44].

Irradiation has a much greater effect on the catalytic activity of insulators, such as alumina, silica gel, magnesium oxide, and alumina–silica. The hydrogen–deuterium exchange reaction is outstanding in its sensitivity to prior irradiation of the catalyst. By using a gamma-irradiated catalyst (e.g. alumina[24,25], titanium dioxide[45], silica gel[36,37,46-53], alumina–silica[54]), the rate of this reaction at 77°K can be increased by several orders of magnitude. A significant increase in reaction rate following irradiation of the catalyst has been observed with magnesium oxide[55], and a somewhat smaller increase with zinc oxide[50].

Irradiation of silica gel[36], magnesium oxide[56,57], and alumina[58] had an appreciable effect on the rate of *ortho–para* hydrogen conversion. Leffler and Ostar[59] found that the rate of this reaction is strongly influenced by prior mixed irradiation (neutrons and gamma rays) of low-activity

catalysts (aluminas with small admixtures of transition-metal salts).

Hentz[60,61] noted a sharp increase in the activity of an alumina–silica catalyst towards the decomposition of isopropylbenzene at room temperature after gamma irradiation.

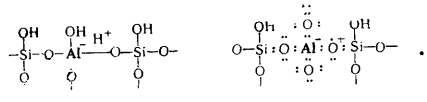
Both increases and decreases in catalyst activity after irradiation have been reported also for reactions of the acid–base type[38,39,60-68]. Particularly interesting in this respect is the work of Mikovsky and Weisz[39], who showed that the catalytic activity of silica gel and alumina–silica samples towards the isomerisation of butene could be increased drastically and stably by prior irradiation in a nuclear reactor using a neutron flux of integrated intensity 10^{20} cm^{-2}, the activity of the silica gel being increased almost 50-fold. Surprisingly, the activity of the catalyst did not fall on heating, suggesting the formation of active centres of the impurity or structural type on irradiation.

Barter and Wagner[67] found that silica gel becomes catalytically active in the isomerisation of cyclopropene and butene after being irradiated with 3 MeV electrons.

The most detailed studies of the hydrogen–deuterium exchange reaction were reported by Kohn and Taylor[24,25,36,37,45-50], and also by Mishchenko and coworkers[51-53]. According to the former, the activity of silica gel increases with content of alumina, probably because the electrons and holes produced by irradiation can be trapped on active centres present in the solid. Kohn and Taylor studied the colour centres and the paramagnetic centres of irradiated silica gel[46-48], and concluded from their results that both the colouration and the appearance of adsorption and catalytic activity after irradiation are associated with the capture of the resulting charge carriers (holes) by impurity atoms (in particular, aluminium). The adsorption centres and the catalytic centres in irradiated silica gel are believed to be of different kind. The authors have not definitely identified the catalytically active centres on the surface of the irradiated catalyst, but they believe that the paramagnetic and the catalytic centres are somehow related.

Kohn and Taylor's conclusion that the specific activity of identically irradiated silica gel samples increases with alumina content has been confirmed[51-53] by independent workers. However, and in contrast to Kohn and Taylor's results, the latter found that the adsorption and catalytic activity in irradiated silica gel change in the same sense as the intensity of the ESR signal on changing the temperature (Fig. 1). This suggests that the surface centres responsible for hydrogen adsorption and for isotope exchange are identical. The formation of these surface centres for adsorption and catalysis is related to the presence of aluminium impurities in the silica gel: the impurity atoms create acidic centres in the surface layer of the silica gel, and the free electrons produced by irradiation are captured by protons with formation of hydrogen atoms.

The charge which appears on an aluminium atom when a proton is expelled under the influence of radiation is compensated by a hole which is stabilised by an oxygen atom adjacent to the aluminium atom:



The correlation between the formation of colour centres during irradiation of alumina–silica catalysts and the appearance of catalytic activity was stressed also by Hentz[69], who studied the decomposition of isopropylbenzene on previously gamma-irradiated alumina–silica catalysts of different composition. He concluded that activation centres created by the irradiation and related to solid-state defects are the source of energy for the decomposition of isopropylbenzene with formation of benzene, unsaturated hydrocarbons, and hydrogen. Aluminium atoms, which can trap a positive hole, play the role of defects in alumina–silica catalysts. Other centres, unrelated to colour centres, but active towards the dealkylation of isopropylbenzene, have been postulated in addition to these activation centres.

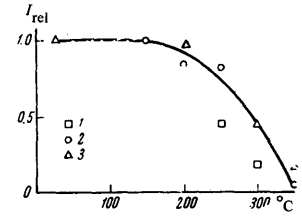


Figure 1. Catalytic activity (*1*), intensity of the sextet in the ESR spectrum (*2*), and adsorption capacity (*3*) of irradiated silica gel, in relative units, as a function of vacuum baking temperature[51].

Lunsford and Leland[55,57] explained the increased catalytic activity of magnesium oxide towards the hydrogen–deuterium exchange and *ortho–para* hydrogen conversion reactions after neutron irradiation, and also the appearance of an ESR signal, in terms of a change in the electronic structure of magnesium oxide. They postulate the formation of electron traps consisting of radiation defects but similar to impurity defects such as tervalent iron cations.

Studies of the action of radiation on alumina–silica butene isomerisation catalysts[65], and of the cracking of isopropylbenzene on alumina–silica after irradiation with protons or gamma rays[70], have revealed parallel changes in catalytic activity and in the strength of the ESR signals from paramagnetic centres.

Sazonov and coworkers[71] showed that prior irradiation of rare-earth oxides (lanthanum, samarium, gadolinium) increases the rate of oxygen isotope exchange by two orders of magnitude. Catalytically active centres are assumed to be formed during irradiation by the trapping of free electrons on anion vacancies. The analogy between the active centres formed by heat treatment in a vacuum and those found in irradiated samples was stressed[72], and it was suggested that the active centres in both cases are metal ions associated with an oxygen vacancy, since the binding energy of an excess electron is different at these sites.

Thus, summarising the results of various investigations, we note that the most widely held view of the nature of the catalytically active centres produced in insulating and in semiconducting oxide catalysts by irradiation is that the centres consist of electric charge carriers localised on various types of surface defects. The active centres created by irradiation can be analogous to the active centres which operate in ordinary catalytic reactions.

The use of ionising radiation offers new methods of creating active centres and of studying their nature and their role in catalytic and chemisorption processes. The

most stable active centres appear, as a rule, in insulators, which are characterised by a wide forbidden gap.

III. FEATURES OF CATALYTIC REACTIONS TAKING PLACE UNDER THE INFLUENCE OF IONISING RADIATION

The width of the forbidden gap of the catalyst, the main factor in determining the stability of radiation-induced catalytic centres, is particularly important in catalytic reactions taking place under the influence of radiation, since in this case the elementary act of a multistage radiation–catalytic reaction can involve the less active centres as well: electrons and holes held in "shallow" traps, and free excess carriers.

The lifetime of radiation-induced defects in a solid is a very sensitive function of temperature for a given set of irradiation conditions. Therefore, catalytic reactions with simultaneous irradiation can be divided into two groups: those taking place at relatively high temperatures, such as are used in ordinary catalysis, and reactions carried out at low temperatures, whose rate would be negligibly small but for the influence of radiation.

1. Catalytic Reactions Under the Influence of Radiation at High Temperatures

In radiation–catalytic reactions at temperatures high enough for the rate to be appreciable even in the absence of radiation, the effect of the radiation is to contribute an additional term to the overall reaction rate. A critical temperature can usually be found, depending on the nature of the reaction, of the catalyst, and of the radiation, above which the radiation ceases to have any effect and the contribution of the radiation term to the overall reaction rate practically vanishes. A similar relationship is found also in studies of the effect of radiation on the electrophysical properties of solids. Unfortunately, no simultaneous studies of the effect of temperature on the electrophysical properties and on the catalytic activity of solids in radiation–catalytic reactions appear to have been made. Data of this type would be very difficult to obtain with the highly disperse solids used as catalysts.

Direct measurements of the radiation component of electrical conductivity, taken under irradiation conditions, have been published. Figs. 2 and 3 give the results of measurements of the electrical conductivity as a function of temperature on quartz[72] and potassium iodide[4], both of which are wide-gap materials. It is evident that the radiation component of the conductivity vanishes at ~140° for both quartz and monocrystalline potassium iodide.

Barry and Roberts[73] found that the rate of the synthesis of methanol from carbon monoxide and hydrogen over zinc oxide (in a flow system at atmospheric pressure) is increased by a factor of 2–3 by gamma radiation at 160–230°, whereas above 230° the radiation has no effect.

The decomposition of methanol on zinc oxide[74] is also markedly accelerated by gamma radiation provided the temperature is below 400°. Above this temperature no radiation effect could be detected.

A peculiar difference in the effect of radiation on the activity of *n*- and *p*-type semiconductors was noted in the same paper[74]. With zinc oxide (an *n*-type semiconductor) the rate of decomposition of methanol was increased by irradiation, but with chromium oxide (a *p*-type semiconductor) the opposite effect was observed under otherwise identical experimental conditions. Evidently, this effect is due to some specific feature of the methanol decomposition mechanism, in conjunction with the electronic structure of the catalysts. As the authors point out, the effect of the radiation decays rapidly when the catalyst is shielded from the source of radiation. There is an interesting "saturation" effect, or some kind of limit to the effect of radiation on the catalytic activity of zinc oxide and chromium oxide samples of different initial activity. The radiation–catalytic activity of the samples of zinc oxide and chromium oxide found to be most active in the ordinary catalytic reaction was independent of the radiation dose. On the other hand, the radiation–catalytic activity of low-activity zinc oxide could be made to approach the activity of the most active zinc oxide sample in the non-irradiated state at high enough doses. This observation is consistent with the hypothesis put forward by Coekelbergs and coworkers[22], according to which radiation can have no effect on a semiconductor already carrying a maximum concentration of current carriers.

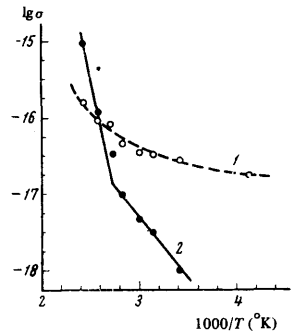


Figure 2. Temperature dependence of the logarithm of the electrical conductivity of crystalline potassium iodide[4]: *1*) not irradiated; *2*) exposed to X-rays.

The radiation–catalytic oxidation of carbon monoxide on alumina[75] under the influence of X-rays has been studied by the dynamic method over the temperature range 23–400°. The effect of irradiation was to increase the reaction rate at temperatures up to 300°.

It has been shown that the activation energy of the reaction is zero in the temperature range 80–300°. At temperatures above 300°, however, the activation energy is 18 kcal mole^{-1}, i.e. is almost indistinguishable from the activation energy of the thermal reaction (Fig. 4).

Spitsyn and coworkers[76–83] have studied catalytic reactions at very high temperatures using radioactive catalysts. These systems are much more complex and specific, because the source of radiation in this case is a radioactive isotope of one of the elements in the crystal lattice of the catalyst. They found that the catalytic activity of sodium and magnesium sulphates and of tricalcium phosphate containing ^{35}S, ^{45}Ca, and ^{32}P towards the dehydration of cyclohexanol and isopropanol increases with the specific radioactivity of the catalyst and with the intensity of β-radiation. The introduction of radio-isotopes into the catalyst led in some cases[76,77] to a fall (100–120 deg) in the optimum temperature for the reaction. According to the authors[14,80,81], these effects can be explained by the charging of the sample.

It must be stressed that the catalytic activity of radioactive catalysts is very dependent on the method of preparation. Spitsyn ascribes[83] to this effect the discrepancy between the results obtained in his laboratory and those of Krohn and Smith[84].

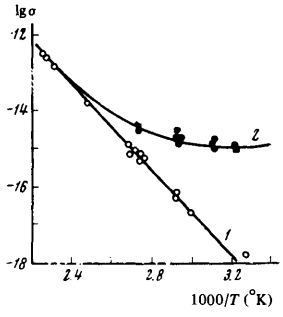


Figure 3. Temperature dependence of the logarithm of the electrical conductivity of quartz[72]: *1*) not irradiated; *2*) exposed to radiation.

In another series of papers[85-88] Spitsyn and coworkers discuss the dehydration of n-decanol and the isomerisation of dec-1-ene over aluminium oxide at 250–450° under the influence of various types of radiation: X-rays, gamma rays, and radiation from a nuclear reactor. The highest increase in reaction rate (a factor of 2–3) was obtained using X-rays. Irradiation with gamma rays and with neutrons lowered the catalytic activity of the alumina: according to the authors, this is explained by the annihilation of active centres on the catalyst surface. The rate of isomerisation was increased by irradiation with sources of all types except gamma rays from ^{60}Co, which caused a decrease in the rate of isomerisation of dec-1-ene. A decrease in the optimum temperature was found also on adding ^{137}Cs as a radioactive impurity. The effect of radiation decreased on raising the temperature of the catalytic reaction, obviously as a result of "annealing" of the radiation defects. The same effect of temperature on the radiation-catalytic activity was found by Maxim and coworkers[89] in their work on the oxidation of carbon monoxide on nickel oxide containing 2.5% of lithium in the presence of radiation. With catalysts of relatively low initial activity and conductivity, and at low reaction temperatures, irradiation had a drastic effect on both the catalytic activity and the electrical conductivity of the system.

Thus, existing data indicate that changes in catalytic activity during radiation-catalytic processes are usually relatively minor, they are most likely to be found at low temperatures, and they vanish completely at high temperatures.

2. Low-temperature Radiation-Catalytic Reactions

This group of reactions includes, mainly, radiation-catalytic reactions in the adsorption layer, which are carried out at low temperatures, where the rate of the normal catalytic reaction is negligible. In this case the radiation effect is all-important, because the ionising radiation is the only source of energy available to low-temperature radiation-catalytic reactions. The "Arrhenius" activation energy for these reaction is usually almost zero.

The most characteristic feature of these reactions is the transfer of the energy absorbed by the solid to molecules adsorbed on its surface. The transfer of energy supplied by the ionising radiation from the solid to the adsorbed molecules is confirmed by a fund of experimental evidence, according to which the radiation-chemical yield of heterogeneous reactions (calculated for the adsorbed species) is well in excess of the corresponding radiation-chemical yield for the homogeneous reaction.

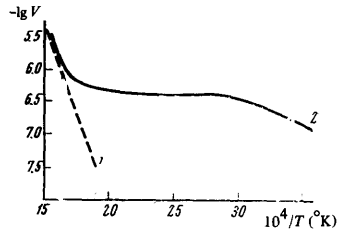


Figure 4. Logarithm of the catalytic activity of Al_2O_3 (V) against reciprocal temperature for the oxidation of carbon monoxide[75]: *1*) dark reaction; *2*) exposed to radiation.

We must stress that the radiation-chemical yields of heterogeneous catalytic reactions are very difficult to compute, because of the need to know the distribution of the energy absorbed by the system between the catalyst and the adsorption layer, the mechanism of transfer of the absorbed energy, etc. With radiation-catalytic reactions in the adsorption layer it can be assumed that the energy of the ionising radiation is absorbed by the solid and by the adsorbate in proportion to their electron fractions. In practice, the radiation-chemical yield of a reaction involving the adsorbate can be defined in two ways: the radiation-chemical yield referred to the energy absorbed by the whole system, i.e. solid and adsorbate, and the radiation-chemical yield referred to the energy absorbed by the adsorbate only, G_{ads}‡. The latter does not reflect the true significance of the radiation-chemical yield. However, a comparison of G_{ads} with the corresponding radiation-chemical yield for the homogeneous radiolysis (G_{hom}) leads to some definite conclusions on the role of the solid in the radiation-catalytic reaction and on the ways in which energy absorbed in the bulk of the solid can be transferred to molecules adsorbed on its surface. Radiation-chemical yields per 100 eV of energy absorbed by the whole system are termed G_{tot}, as in a number of other investigations[22]. Large values of this yield (upwards of 100) are evidence that a chain mechanism may be present. The radiation-chemical yield G_{tot} is a measure of the extent to which the radiation energy absorbed by the whole system is utilised.

The chemical nature, and in particular the electronic properties of the solid, play an important role in the energy transfer process. Some solids can accelerate chemical

‡ This quantity is sometimes termed G_{gas} in the foreign literature[22].

processes on their surface, i.e. they are radiation catalysts and they provide an effective medium for the energy transfer; other solid are altogether lacking in these properties. The earliest investigations of the role of the catalyst in the energy transfer process were aimed at the heterogeneous radiolysis of alkanes. Allen and coworkers[90-94] studied the influence of gamma radiation on the low-temperature reactions of pentane adsorbed on silica gel, alumina, magnesium oxide, and various molecular sieves. The relationship between the radiation-chemical yield of hydrogen and the electron fraction of pentane adsorbed on solid surfaces led the authors to propose an energy transfer effect between the solid and molecules adsorbed on its surface. The energy transfer was assumed to be confined to the first adsorbed layer, the rate of the heterogeneous reaction in all other layers being the same as that for the homogeneous reaction.

A large number of products, of different composition, have been detected during the radiation-induced conversion of pentane in the adsorbed state, the most abundant being hydrogen and decane isomers. In contrast to the homogeneous radiolysis of pentane, the yields of unsaturated hydrocarbons were quite low and the yields of isomerisation products were high, suggesting that the selectivity of the reaction had been changed. The radiation-chemical yields were dependent on catalyst composition and (for catalysts of a given composition) on the particle size. Fig. 5 shows the dependence[91] of radiation-chemical yield on the coverage of the adsorbent surface. Radiolysis measurements on NaCoX molecular sieve failed to detect any hydrogen formation on this catalyst.

However, the curves of Fig. 5 relate to the formation of free hydrogen, and may be significantly distorted by radiation-induced hydrogen chemisorption, known to occur to different extents on different solids[95-97].

The authors discuss these results from the standpoint of electronic ideas, the energy transfer process being treated as the motion and recombination of free electrons and holes formed by irradiation.

Topchiev and his coworkers[98-102] studied the heterogeneous radiolysis of heptane adsorbed on aluminium silicate, chromate, molybdate, and other oxide catalysts under the influence of gamma radiation. The reaction was investigated both at room temperature and at liquid nitrogen temperature. The composition of the heterogeneous radiolysis products of heptane differed from the composition of the homogeneous radiolysis products; the heterogeneous catalytic reaction gave fewer unsaturated hydrocarbons and a greater proportion of isomerisation products, again showing that the selectivity of the process had changed. The investigation included a study of the effect of coverage on the reaction rate. The transfer of energy from the solid to the adsorbed molecules, first established by Allen, was confirmed in this work. It was also shown that the rate of radiolysis of hydrocarbon adsorbed in excess of monolayer coverage was the same as the rate of the homogeneous reaction[99]. The rate of the heterogeneous radiolysis of heptane fell steeply at high doses (of the order of 5×10^8 rad); one possible explanation is rapid polymerisation of the resulting unsaturated compounds.

Hentz[103] studied the effect of radiation on the reactions of isopropylbenzene adsorbed on microporous alumina-silica. The following species were detected among the decomposition products: hydrogen, methane, propene, propane, isobutane, benzene, isopropylcyclohexane, etc. The reaction was found to be more specific than the radiation-induced decomposition of liquid or gaseous isopropylbenzene. Thus, the yield of benzene was higher in the presence of the catalyst, the formation of unsaturated hydrocarbons was inhibited, the amount of isomerisation products increased, and isopropylcyclohexane could not be detected in the absence of the catalyst. The radiation-chemical yields of all products decreased at higher doses of absorbed radiation. By studying the dependence of the individual yields on the electron fraction of the particular adsorbate the author concluded that the mechanism of benzene formation is different from that of all the other products. Whereas the yield of methane increased slowly with the electron fraction of isopropylbenzene (in the low-coverage region), and the yield of hydrogen fell, the yield of benzene went through a sharp maximum at 1% coverage of the surface. This behaviour was ascribed to saturation of the centres most active towards dealkylation. In the light of the peculiar relationship between the benzene yield and coverage, and of the high radiation-chemical yields in the presence of the solid, the author concludes that the energy absorbed by the solid is transferred to the adsorbed molecules and is converted into the energy needed to activate the chemical reaction.

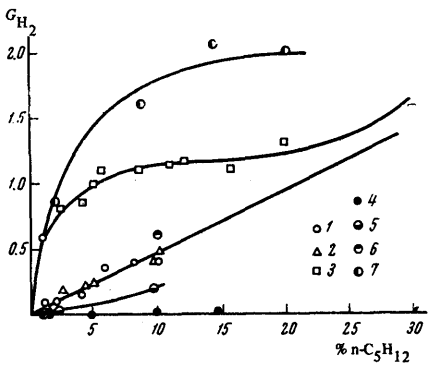


Figure 5. Hydrogen yield as a function of n-pentane adsorbed (wt.%)[91]: *1*) SiO_2 (100 μm); *2*) SiO_2 (62 μm); *3*) SiO_2 (0.02 μm); *4*) Fe_2O_3 (less than 44 μm); *5*) attapulgite (1 μm); *6*) montmorillonite (5 μm); *7*) silica gel.

There have been several recent reports of the effect of radiation on the reactions of inorganic and organic compounds adsorbed on various substrates. The yields are invariably higher than those of the corresponding homogeneous reactions.

The heterogeneous radiolysis of carbon dioxide has been studied by a number of workers. Thus, Coekelbergs and coworkers[104] investigated the radiation-chemical decomposition of carbon dioxide adsorbed on alumina, silica gel, and magnesium oxide under the influence of gamma radiation from ^{60}Co, beta radiation from ^{90}Sr, and X-rays. Energy transfer from the solid to the adsorbed molecules was confirmed in every case. With alumina, the ratio G_{ads}/G_{tot} increased very markedly at lower surface coverages. The radiation-chemical yields remained constant in the temperature range 25-300°, and the nature of the radiation also had little effect.

Other workers[105] studied this reaction on silica gel, alumina, and various semiconductors. The radiation-chemical activity was higher with intrinsic semiconductors than with n- or p-type semiconductors. Changes in dose rate over the range 0.28–3.18 Mrad h^{-1}, and temperature increase up to 180°, had no effect on the radiation-catalytic process.

Sutherland and coworkers[106] studied the rate of radiolysis of carbon dioxide adsorbed on silica gel as a function of the dose of radiation, of the concentration of adsorbed molecules, of the catalyst preparation conditions, and of the water content in the silica gel. The high radiation-chemical yields of carbon monoxide were ascribed to energy transfer from the sorbate to the sorbent (sic.).

One of the earliest papers from Coekelbergs' laboratory[107] discusses the decomposition of nitrous oxide at 80°, with formation of nitrogen and oxygen, in the presence of silica gel or alumina and under the influence of fission products. The microporous sorbents were found to increase the ratio G_{ads}/G_{hom} by a factor of 3–10. Nitrogen fixation was also investigated (at 25 atm and 80°, in the presence of fission products). The total amount of fixed nitrogen was defined as the sum of the oxides $NO_2 + N_2O_3 + N_2O_5$. The reaction was shown to be strongly influenced by the presence of microporous solids, especially silica gel.

Coekelbergs and coworkers[108] studied the synthesis of ammonia on alumina at atmospheric pressure under the influence of beta rays from ^{90}Sr and gamma rays from ^{60}Co: the former had little effect, but in the presence of gamma radiation the yield of ammonia was proportional to the dose of radiation, independent of hydrogen pressure, but dependent on the pressure of nitrogen. The activation energy in the range 200–600°K was found to be ~0.5 kcal $mole^{-1}$, with a radiation-chemical yield G_{ads} of 100–500 molecules. This high value of G_{ads} is ascribed to the transfer of the energy absorbed by the solid to the adsorbed molecules. Ammonia synthesis occurred on one grade of alumina only: no reaction was observed on the other alumina samples, or on silica gel, magnesium oxide, and zinc oxide.

Thus, the most marked effect of ionising radiation on the reactions of adsorbed molecules is found with solids of the insulator type, which have also been most extensively investigated. Semiconductors have been studied in a few isolated cases in this context, metals hardly at all.

The radiation-catalytic activity of solids with different gap widths (insulators, semiconductors, and metals) was first investigated under otherwise identical experimental conditions by Zhabrova and her coworkers[109,110], who chose cyclohexane in the adsorption layer as their experimental system. Irradiation was by fast electrons and by gamma rays from ^{60}Co. The most active catalysts were found to be insulating oxides (silica gel, alumina-silica, and alumina), whereas metals and low-gap semiconductors (such as zinc oxide, cuprous oxide, nickel oxide, and active carbon) did not develop catalytic activity on irradiation. The radiation-chemical yield of hydrogen was studied as a function of surface coverage of silica gel by cyclohexane (Fig. 6), and it was found that the extent of reaction of cyclohexane with formation of hydrogen increases with decrease of coverage. A possible energy transfer mechanism from the solid to the adsorbed molecules was put forward on the basis of the band theory of the solid state. It must be stressed, however, that in this work the radiation-catalytic activity was determined merely from the amount of hydrogen evolved. Hence, the quantitative data for the radiation-chemical activity of the various solids obtained in this work may be in error by the extent to which hydrogen is adsorbed on these solids.

This deficiency was overcome in a study by the same authors[111-114] of the radiation-catalytic reactions of methanol adsorbed on solids with forbidden gaps of different width. In this work the radiation-catalytic activity was determined for all the main reaction products: hydrogen, formaldehyde, and ethylene glycol. The highest radiation-chemical yields G_{ads} were obtained with insulators (high energy gap materials). Thus, with silica gel the parameter G_{ads} exceeded the corresponding radiation-chemical yield for the homogeneous radiolysis of methanol by over a factor of 10. Significant radiation-catalytic activity was found also in alumina, alumina-silica, and potassium fluoride, whereas semiconducting oxides had lower activity. Metals, active carbon, and graphite showed no radiation-catalytic activity.

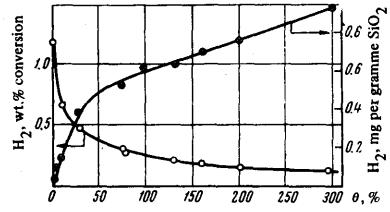


Figure 6. Amount of hydrogen formed and percentage conversion of cyclohexane against coverage of a silica gel surface by cyclohexane[110].

The fact that the radiation-chemical yields of the products of the heterogeneous radiolysis of methanol are much higher on the surface of insulators and some semiconductors than the radiation-chemical yields of the corresponding homogeneous reaction suggests that these solids are able to transfer the energy absorbed from the ionising radiation to molecules adsorbed on their surface. This is evidently not the case for the other group of solids (platinum, palladium, cuprous oxide, nickel oxide, active carbon, and graphite).

Rabe and coworkers[115] studied the radiolysis of azoethane adsorbed on silica gel. Only the gaseous decomposition products were monitored, consisting mainly of nitrogen (with small amounts of hydrogen and methane). The higher yield of nitrogen (as compared with the homogeneous reaction) is explained by assuming that the radiant energy absorbed by the solid is used in the chemical decomposition of the adsorbed azoethane. A more recent communication by the same authors[116] describes the radiolysis of azoethane adsorbed on different solids: silica gel, magnesium oxide, zinc oxide, nickel oxide, titanium dioxide, alkali metal halides, and graphite. The conclusion is that, as in the radiation-catalytic decomposition of cyclohexane and methanol, the strongest tendency to transfer absorbed energy from the solid to molecules adsorbed on the surface is found in insulators. Some semiconductors have a weak effect, others have practically none. The relative radiation-catalytic activity of solids towards the radiolysis of azoethane is illustrated in Fig. 7 as plots of amount of nitrogen formed against surface coverage of the solids by azoethane. With the exception of magnesium oxide, the amount of nitrogen increased monotonically in every case with surface coverage. With magnesium oxide the relationship was more complicated, with maxima at

different coverages for the various products. The radiation-chemical yield of the decomposition products of azoethane decreases with increasing dose of total absorbed radiation.

Sorokin and coworkers[117-119] made a detailed study of the decomposition of ammonia adsorbed on various zeolite surfaces, and found that when the Na form of the zeolite is used the radiant energy absorbed by the solid is transferred to the adsorbed ammonia molecules. The yield of hydrazine—the main radiolysis product of ammonia—expressed in terms of the energy taken up by the adsorbed ammonia was considerably higher than the corresponding yield for the radiolysis of liquid or gaseous ammonia. The radiation-chemical yields of products increased at lower surface coverages of the zeolite by ammonia, and the ratio of hydrazine to hydrogen increased, showing that the selectivity of the process had changed. No energy transfer was observed on irradiating ammonia adsorbed on zeolite in the Ca form.

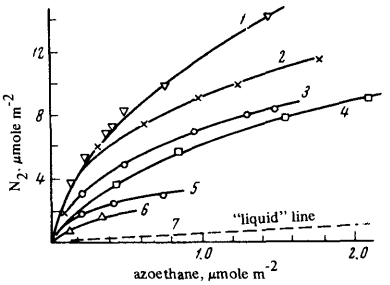


Figure 7. Nitrogen evolved against adsorption of azoethane on various solid surfaces[115]: *1*) SiO_2 (5.9 Mrad); *2*) KI (2 Mrad); *3*) NaF (2 Mrad); *4*) NaCl (2 Mrad); *5*) LiF (2 Mrad); *6*) SiO_2 (1.5 Mrad); *7*) homogeneous radiolysis ("liquid" line).

The influence of the ions present in the zeolite structure on the radiation-catalytic properties of the system has been noted also in the radiolysis of pentane[93] and cyclohexane[120] in the adsorption layer.

The radiolysis of water adsorbed on silica gel has been studied by Krylova and Dolin[121]. The high radiation-chemical yield of hydrogen (calculated on the basis of the energy taken up by the adsorbed water only) is explained by postulating that the adsorbed molecules can acquire additional energy from the solid. The effect of adsorbed water on the ESR spectrum of silica gel irradiated at −196° supports the energy transfer hypothesis. Carbon dioxide was detected among the radiolysis products: according to the authors, this is the result of interaction between traces of residual organic matter on the silica gel surface and oxidising agents formed during the radiolysis of water. More rigorous purification of the silica gel surface from traces of organic compounds lowered the radiation-chemical yield of the radiolysis products of water.

As was pointed out above, there is ample evidence[110,113,116] that, in contrast to ordinary catalysis, the solids most active in radiation-catalytic processes are insulators and wide-gap semiconductors. The dependence of catalyst activity upon the width of the forbidden gap for radiation-catalytic and ordinary catalytic reactions is shown in Figs. 8 and 9. Fig. 8, which refers to the radiation-catalytic decomposition of methanol, shows that semiconductors and insulators behave as active catalysts if their forbidden gap is 4 eV wide or more. We note that the acid-base properties of the solids do not appear to play an important part in radiation-catalytic processes: it can be seen from Fig. 8 that insulators with acidic properties (SiO_2, Al_2O_3) are as effective as basic insulators (MgO, CaO) towards the radiation-catalytic reactions of methanol.

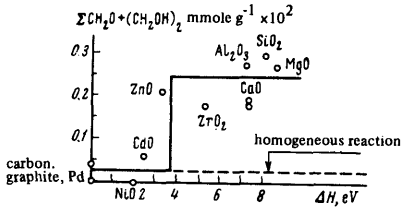


Figure 8. Radiation-catalytic activity of solids as a function of forbidden gap width[122].

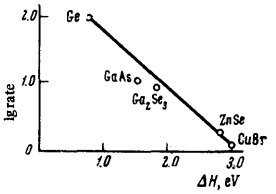


Figure 9. Activity of semiconductor catalysts as a function of forbidden gap width[123].

In contrast to radiation catalysis, the activity of the catalyst in ordinary oxidation-reduction catalysis decreases as the width of the forbidden gap increases[123].

Coekelbergs and coworkers[16] have shown theoretically that large qualitative and quantitative changes in catalytic activity can be obtained even at low radiation intensities in the case of insulators. On the other hand, only minor changes in activity are possible (even at high radiation intensities) in the case of "good" semiconductors. This behaviour is sometimes found also with radiation-catalytic chain reactions. Thus, the radiation-chemical yield for the polymerisation of ethylene (in terms of the energy absorbed by the whole system) is 20–50 times higher on silica gel, alumina, or zeolites than in the homogeneous reaction. The lowest catalytic activity was that of the semiconductor zinc oxide, whereas active carbon actually inhibited the reaction.

The rate of the radiation-catalytic polymerisation of acrylonitrile and methyl methacrylate at −78° increased by an order of magnitude in the presence of magnesium oxide and some *p*-type semiconductors[125], whereas *n*-type semiconductors were less effective. The polymers obtained by this reaction had a high molecular weight, a high density, and a stereoregular structure.

A group of workers[126,127] has studied the radiation-induced graft polymerisation of methyl methacrylate and styrene on powdered magnesium oxide and Aerosil (SiO_2). The rate of the reaction was found to depend on the monomer concentration in the adsorption layer. The high radiation-chemical yield of the reaction is ascribed by the authors to transfer of the energy absorbed by the catalyst to the surface.

The radiation-catalytic synthesis of higher carboxylic acids from ethylene and carbon dioxide has been achieved in the presence of an insulator (alumina)[128,129]. The consumption of ethylene, related to the total energy absorbed, was $G_{(-C_2H_4)} = 10^3$. The carboxylic acids contained approximately 100 molecules, i.e. the yield of radiation-induced polymerisation centres was about 10. The catalyst appears to act not only by increasing the initiation efficiency but also by partly suppressing the chain-breaking step. In the absence of radiation the reaction did not take place, even on adding free-radical initiators.

The radiolysis of heptane in the adsorption layer on alumina above 150° is also stated to be a chain reaction[101].

Kohn has made a detailed study of the radiation-catalytic oxidation of approximately 70 different hydrocarbons on silica gel and alumina[130]. The radiation-chemical consumption of oxygen was often very high, with $G_{(-O_2)} \simeq 100$, suggesting the possibility of chain reactions. The yield of reaction products was independent of temperature, and increased on lowering the oxygen pressure. According to the author, existing views on the mechanism of chain growth on the surface for "dark" heterogeneous reactions cannot explain the growth of chains during the radiation-catalytic oxidation of hydrocarbons. Radiation-catalytic chain reactions are characterised by a very high radiation-chemical yield (on the basis of total absorbed energy). One possible explanation is more effective chain initiation at the surface of an irradiated solid, coupled with a lower mobility of the growing molecules in the adsorption layer of a solid surface. The latter effect can inhibit the rate of chain breaking. Also, the "orientation" of the molecules on the surface of a solid can influence the mechanism of chain growth, and sometimes leads to the formation of stereoregular polymers[125] as in the case of thermal heterogeneous polymerisation.

3. Possible Mechanism and Electronic Steps in the Radiation-induced Transformation of Adsorbed Molecules

As was stated above, in radiation-catalytic processes the radiant energy absorbed by a wide-gap solid can be transferred to chemisorbed molecules, the result being a radiation-chemical yield G_{ads} of reaction products much greater than the corresponding yield for homogeneous radiolysis.

Early workers used the statistical approach to explain the main features of energy transfer[98,102]. According to others[131], the radiation-catalytic activity of solids is determined by their specific heat, the more active catalysts having relatively low specific heats. These ideas have not been confirmed experimentally. Various reaction schemes involving surface hydrogen atoms are considered in a series of investigations of the radiation-catalytic activity of silica gel. One such scheme was proposed by Sutherland and Allen[94] in order to account for the selectivity of the heterogeneous radiolysis of pentane on the surface of silica gel and on NaHX molecular sieve:

$$SH \rightsquigarrow S + H \quad (1)$$

$$H + C_5H_{12} \rightarrow C_5H_{11} + H_2 \quad (2)$$

$$C_5H_{11} + C_5H_{11} \rightarrow C_{10}H_{22} \quad (3)$$

where SH is a surface compound with Si-OH groups.

In the liquid-phase radiolysis the yield of decane is 1/2, consisting almost entirely of isomeric decanes. If silica gel is used the yield of decane becomes 2/3, of which 1/6 is n-decane and the remaining 5/6 are a mixture of isomers. With NaHX at low coverages, a higher ratio of decane isomers to normal decane is obtained.

According to Sutherland and coworkers[106], during the heterogeneous radiolysis of carbon dioxide on silica gel energy is absorbed also by surface Si-OH groups, which then interact with adsorbed molecules. It must be noted, however, that schemes involving OH groups of the silica gel are usually supported only by indirect evidence. Strelko and Suprunenko[132] observed the formation of $\cdot C_6H_6D$ and $\cdot C_6H_7$ radicals during isotope exchange between the hydrogen atoms of benzene adsorbed on silica gel and partially deuteriated OH groups, under the influence of ionising radiation.

Unambiguous proof of the participation of silica gel surface groups in radiation-catalytic reactions of organic compounds obviously requires a study of hydrogen exchange between the surface groups and the reacting molecules during the radiolysis.

On the other hand, studies of the radiation-catalytic reactions of methanol on silica gel have shown unequivocally that surface hydrogen atoms are not involved in the reaction, since the radiation-catalytic activity of silica gel is not affected when the hydrogen ions of OH groups are replaced by calcium ions[136].

Electronic models are widely used to explain the features of energy-transfer phenomena in radiation-catalytic reactions.

Caffrey and Allen[91], in their work on the heterogeneous radiolysis of pentane on silica gel and on molecular sieves, discussed a possible mechanism for the transfer of absorbed energy from the solid to adsorbed molecules, involving the recombination of electrons with positive charges localised on adsorbed molecules. The authors postulated the formation of a pentyl radical.

ESR studies of the radiation-catalytic reactions of cyclohexane[110] revealed the formation of adsorbed $\cdot C_6H_{11}$ radicals and the appearance of paramagnetic centres on the surface of the insulating oxides and fairly-wide-gap semiconductors which catalyse this reaction. No adsorbed $\cdot C_6H_{11}$ radicals or paramagnetic centres were observed with semiconductors lacking radiation-catalytic activity towards the reaction. The cyclohexane was assumed to be adsorbed on an excess charge carrier (hole) with formation of a positively charged molecule of cyclohexane. Recombination of an electron from the conduction band can take place on this charged molecule, and the recombination energy, determined by the width of the forbidden gap, is localised on the adsorbed molecule and enables it to decompose. There is a high probability that the decomposition is accompanied by the formation of free radicals, but the composition of the radiation-catalytic decomposition products of cyclohexane is so complicated that it was not possible to compare the amounts of products and radicals formed and to establish the role of the latter in the overall process.

The mechanism of the radiation-catalytic transformation of methanol has been studied in greater detail[111-113]. Irradiation of methanol adsorbed on insulators and on semiconductors showing radiation-catalytic activity leads to the formation of adsorbed $\cdot CH_2OH$ radicals and much smaller

amounts of·CHO and·CH_3. A typical ESR spectrum of irradiated methanol adsorbed on silica gel is shown in Fig. 10. In order to characterise the role of adsorbed radicals, the amounts of radicals and of radiation–catalytic decomposition products of methanol were compared in a special series of experiments. The results (Fig. 11) show the variation of the numbers of resulting ethylene glycol molecules (upper curve) and·CH_2OH radicals (lower curve) with the dose of radiation absorbed. It can be seen that the two curves deviate in the region of high absorption, evidently due to radical recombination at high concentration, whereas in the low-absorption region the curves are close together. This suggests that·CH_2OH radicals are intermediate products in the formation of ethylene glycol. Analogous investigations of the role of·CHO radicals[122] showed that these are not intermediates, but they probably arise by the decomposition of formaldehyde under the influence of radiation.

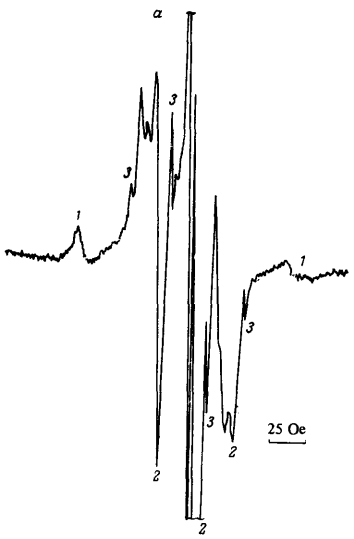


Figure 10. ESR spectrum[113] of methanol adsorbed on silica gel and irradiated at −196° (dose: 10 Mrad): *1*)·CHO radical; *2*)·CH_2OH radical; *3*)·CH_3 radical.

The correlation between the radiation–catalytic activity of solids in the heterogeneous radiolysis of methanol and their electronic properties (forbidden gap width), and also the correlation with the appearance of adsorbed radicals, justify the assumption that the heterogeneous radiolysis of methanol involves both electronic and radical steps, and that the energy transfer process is associated with the motion and recombination of excess charge carriers generated in the solid by the radiation. From the experimental results, the following scheme was put forward for the radiation–catalytic conversion of methanol adsorbed on solid surfaces:

$$\text{T solid} \rightsquigarrow \text{T solid} \oplus \ominus$$
$$CH_3OH \oplus \longrightarrow \underset{\text{chem.ads.}}{CH_3OH^+}$$
$$\underset{\text{chem.ads}}{CH_3OH^+} + \ominus \longrightarrow \dot{C}H_2OH + \dot{H}$$
$$\dot{C}H_2OH + \dot{C}H_2OH \longrightarrow (CH_2OH)_2$$
$$\dot{C}H_2OH \longrightarrow CH_2O + \dot{H}$$
$$\dot{H} + \dot{H} \longrightarrow H_2$$

Under the influence of radiation, excess non-equilibrium charge carriers (electrons and holes) are formed in the solid. Methanol molecules adsorbed on the surface interact with these carriers, and since alcohols have electron-donating properties we may assume that the methanol molecules interact with holes. As in the case of cyclohexane, an adsorbed positively charged methanol molecule acts as a recombination centre for an excess electron from the conduction band. Recombination of a pair of charges liberates an amount of energy equal to the width of the forbidden gap minus the height of the energy level of the chemisorbed molecule. If this energy is high enough (≥4 eV), an atom of hydrogen is eliminated from the methanol molecule with formation of a·CH_2OH radical. Recombination of the·CH_2OH radicals produces ethylene glycol molecules, and dissociation of these radicals produces formaldehyde molecules. A hydrogen molecule is formed by the recombination of two hydrogen atoms.

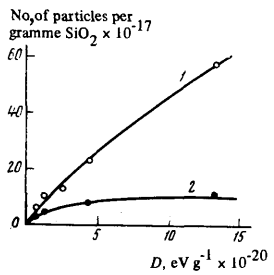
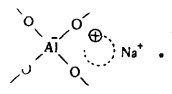
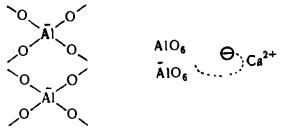


Figure 11. Number of·CH_2OH radicals and of ethylene glycol molecules (expressed as CH_2OH particles) as a function of dose absorbed; surface coverage of silica gel 30% at −196°:[113] *1*) $(CH_2OH)_2$; *2*)·CH_2OH.

A similar energy transfer scheme involving the recombination of excess current carriers, but with the participation of intermediate charged centres, has been proposed from a study of the heterogeneous radiolysis of ammonia on zeolites[117]. By using the ESR method it was shown that hydrazine is formed through the recombination of $\dot{N}H_2$ radicals. As the number of $\dot{N}H_2$ radicals on the surface increases, the number of paramagnetic centres falls (Fig. 12). In order to explain the mechanism of heterogeneous radiolysis, the ESR spectra of ammonia adsorbed on sodium and calcium zeolites were investigated[119], and it was concluded that the paramagnetic entities obtained by gamma irradiation of these two types of zeolite are different. In the Na form the radiation-induced catalytic centres are, according to the authors, of the *V*-centre type, and are similar to the centres formed by irradiation of silica gel containing alumina:



Irradiation of the Ca-form, on the other hand, is said to produce paramagnetic F-centres consisting of excess electrons localised on Ca–O bonds. According to the authors, these centres have the structure



In both forms of zeolite, the energy absorbed in the bulk of the solid must be re-evolved during recombination of the electrons and holes. In the presence of adsorbed ammonia molecules, which have a high affinity for positive charge because of the unshared electron pair on the nitrogen atom, a donor–acceptor bond is formed between the molecule and the surface. In the case of the Na-form, the holes formed by irradiation reinforce the bond between the ammonia molecule and the surface. On the other hand, with the Ca-form the electrons localised at the surface weaken the bond between the ammonia molecule and the surface, and energy transfer by electron–hole recombination has a low probability. As required by this model, the zeolite in the Ca-form was found to be inactive towards the heterogeneous radiolysis of ammonia.

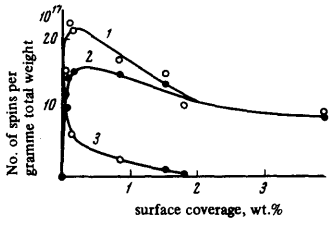


Figure 12. Effect of surface coverage on the concentration of radicals[119]: *1*) total concentration; *2*)·NH_2 radicals; *3*) paramagnetic centres in the zeolite.

Similar recombination mechanisms for the energy transfer process are proposed in other investigations of the radiation–catalytic reactions of organic molecules, recently published[103,117,134]. In most of the schemes put forward a molecule of the organic compound, adsorbed on the surface, acts as the recombination centre for excess current carriers. Intermediate paramagnetic F- and V-centres, formed in the solid during irradiation by capture of an electron or a hole at various defects, are not usually postulated. Yet, these centres must play an important part in processes involving prior irradiation of the catalyst. They stabilise the free current carriers, and thus give rise to "long-lived" excitation in the solid (the "memory" effect). On the other hand, it was shown in a number of investigations that the presence of impurities or other structural defects in the catalyst is relatively unimportant when irradiation is applied during the reaction. For example, the radiation–catalytic activities of silica gel and of alumina–silica containing 10% of alumina were found to be the same in the radiolysis of methanol[111] and of isopropylbenzene[134]. A sample of spectroscopically pure silica gel, containing less than 10^{-4}% of aluminium, had the same radiation–catalytic activity as a sample of silica gel of SMKh grade, containing a significant amount of alumina[122]. Thus, most workers (with the exception of Sorokin[117]) assume that energy transfer in dielectrics involves free charge carriers, and that localised charge carriers (if they are formed) play a minor part. It would appear that direct trapping of excess carriers by adsorbed molecules is the basic process in the radiation–catalytic reactions of adsorbed molecules.

4. Role of the Bulk and Surface of Solids in the Energy Transfer Process

As stated above, the most commonly held view of the energy transfer process involves the recombination of excess non-equilibrium charge carriers formed in the bulk of the solid under the influence of radiation. However, the extent to which these excess carriers from the bulk are used in the radiation–chemical reaction at the surface is still uncertain.

Under these conditions, the radiation-induced chemical reactions of adsorbed molecules offer some insight into the physical processes taking place in the bulk of the solid exposed to ionising radiation. This approach was used by Zhabrova and coworkers[122,135,136], who studied the radiolysis of methanol in the presence of two of the most active radiation catalysts—silica gel and alumina—with different surface-to-volume ratios. The silica gel samples, prepared by the hydrothermal method[137,138], had identical chemical compositions but different specific surface areas and globule diameters D. In the first series of experiments the amount of methanol adsorbed on the samples was the same (0.17 mmole g^{-1}). This amount was sufficient to give monolayer coverage on the sample with the smallest specific surface (20 m^2 g^{-1}), but on the large-area samples the coverage was only a few per cent.

Table 1. Influence of specific surface area and globule diameter of silica gel on the radiation–catalytic decomposition of methanol. Temperature 20°C, dose rate of gamma radiation 1.3×10^{16} eV g^{-1} s^{-1}, dose 10^{20} eV g^{-1}.

Specific surface area S, m^2 g^{-1}	Globule diameter D, Å	Surface coverage θ, %	Amount of products formed, mmole g^{-1} $\times 10^2$		G_{ads}, mmole per 100 eV		Extent of conversion, mole %	
			CH_2O	$(CH_3OH)_2$	CH_2O	$(CH_3OH)_2$	CH_2O	$(CH_3OH)_2$
20	1400	100	0.22	0.12	220	120	1.5	0.8
50	550	51	0.19	0.14	190	140	1.1	0.8
100	270	25.5	0.14	0.10	140	100	0.8	0.6
150	180	17	0.14	0.12	140	120	0.8	0.7
190	140	11	0.16	0.12	160	120	0.9	0.7
350	80	7.2	0.16	0.14	160	140	0.9	0.8
360	75	7.1	0.21	0.12	210	120	1.2	0.7
390	70	6.4	0.21	0.16	210	160	1.2	0.9
540	50	4.7	0.18	0.17	180	170	1.7	1.0
620	40	4.1	0.18	0.18	180	180	1.1	1.0
640	40	4	0.16	0.17	160	170	0.9	1.0
800	30	3.2	0.24	0.18	240	180	1.4	1.0

The results, summarised in Table 1, show that the radiation–chemical yields of products are almost constant for all the samples. Since the methanol undergoes radiation–catalytic reactions only by virtue of the energy transferred from the solid, it is obvious that for a given dose the same amount of energy has been transferred from the bulk to the surface of all the samples examined. The fact

that the energy transferred is independent of the globule diameter of the silica gel and of the surface coverage is evidence that the diffusion of carriers from the bulk to the surface is not rate-limiting, and that the adsorbed alcohol molecules have a fairly large affinity for charge carriers (holes). An analogous series of experiments with alumina samples gave similar results.

In another series of experiments, the adsorption of methanol on the surface of the various samples was varied so as to give a constant surface coverage of 50% of a monolayer. The effect of changing the adsorption of methanol on the surface of one of the samples was also studied. The variation of the radiation-chemical yields of formaldehyde and ethylene glycol with surface concentration of methanol on the silica gel is shown in Fig. 13.

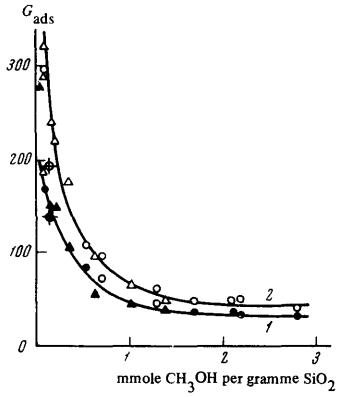


Figure 13. Radiation-chemical yields of oxygen-containing products against adsorption of methanol on the surface of silica gel[136]: *1*) $(CH_2OH)_2$; *2*) CH_2O.

As the Figure shows, the radiation-chemical yields (and therefore also the extents of conversion of the methanol, which are proportional to the yields) for silica gels of different surface areas but constant coverage, and the values for different coverages of the same specimen, all lie on the same curve. The mean of the radiation-chemical yields obtained in the series of experiments of Table 1 also lies on the same curve. For a given dose of absorbed radiation, the highest radiation-chemical yields G_{ads} were obtained on samples with the lowest amount of adsorbed methanol. As the adsorption of methanol was increased, the radiation-chemical yields of both products fell. Thus, this work has shown that the extent of conversion of adsorbed methanol in a radiation-catalytic reaction is determined only by the relationship between the amount of methanol and the number of excess current carriers formed in the bulk of the solid (SiO_2 or Al_2O_3), whereas the specific surface area, the pore size and globule diameter, and the extent of coverage of the surface have no effect on the reaction.

Since all the free charge carriers are effectively captured on adsorbed molecules, irrespectively of the surface coverage, these results justify the conclusion that all or practically all the excess carriers formed in the bulk of the solid are used in the radiation-catalytic process. The values of G_{tot} and G_{ads} (from the sum of the oxygen-containing products), determined from the initial slopes of the kinetic curves, are set out in Table 2. It can be seen that the mean value of G_{tot} for silica gel is 4.4. According to electrophysical measurements[2], the average energy of formation of a pair of charge carriers for a number of insulators is 20 eV. Since this value can be equated to the width of the forbidden gap for insulators, we conclude that the yield of pairs of carriers per 100 eV of energy absorbed in a dielectric of the SiO_2 type should lie between 4 and 5. This agrees satisfactorily with the experimental value of 4.4, thus providing a further argument in favour of the hypothesis that practically all the excess carriers formed in the bulk of a dielectric take part in the radiation-chemical process at the surface.

Table 2. G_{ads} and G_{tot} for the radiation-catalytic conversion of methanol on silica gel at different surface coverages[135].

Coverage, %	G_{ads}, molecules per 100 eV	G_{tot}, molecules per 100 eV
3.8	1970	4.8
17.5	370	4.2
53	120	4.2
100	70	4.4

Further indirect evidence for this conclusion comes from other investigations. Thus, Rojo and Hentz[134] found that the yield of benzene (measured from the initial slope of the kinetic curve) is 4 in the decomposition of isopropylbenzene on silica gel previously irradiated at −196°. In the radiation-catalytic dealkylation of adsorbed isopropylbenzene at room temperature the yield G_{tot} was 2. However, this quantity was determined at a relatively high dose (not from the initial portion of the kinetic curve at low doses), and might therefore be too low. According to the authors, the capture efficiency of current carriers by adsorbed molecules is close to 100%.

Rabe and coworkers[115] obtained curves of the yield of radiolysis products against surface coverage of various solids by azoethane (Fig. 7). In every case (except magnesium oxide) the yield of radiolysis products of azoethane increased with surface coverage up to monolayer coverages, whilst the reaction rate decreased. The authors suggest that the excited species generated in the solid by the radiation have a fairly large radius of action, and that the adsorbed molecules must compete for the energy transferred from the solid.

Thus, the conclusion that the excess current carriers generated in the bulk of the solid are fully utilised in radiation-chemical processes at the surface appears to be generally applicable to all solids of the dielectric type.

It is evident from a survey of published data that the use of ionising radiation in heterogeneous catalysis has opened a new field for the study of electronic factors, which allows the role of free and of localised carriers in the elementary acts of catalytic reactions to be identified, and can suggest ways of controlling these processes.

The use of ionising radiation provides a test of various propositions of the electronic theory of catalysis, and it allows us to formulate new theoretical problems and to extend the range of experimental approaches to the study of elementary acts in catalysis and chemisorption.

The ability of adsorbed molecules to act as "traps" for electrons and holes in competition with other traps (impurities and structural defects on solid surfaces) has been demonstrated by the use of ionising radiation.

It has been amply demonstrated that the creation of charge carriers in insulators and semiconductors often leads to the formation of various kinds of charged and free-radical species on the surface, which play an important part in catalytic and chemisorption processes.

The mechanism of radiation–catalytic reactions is often closely dependent on the transfer of energy absorbed by the solid to molecules adsorbed on the surface. The energy transfer problem is also very relevant in ordinary catalytic reactions, but the elementary mechanism of transfer, involving the motion of electric charges, can differ in the two cases. The width of the forbidden gap is an important consideration in catalysts for ordinary oxidation–reduction reactions. This factor is of major importance also in radiation–catalytic reactions. However, in contrast to ordinary catalysis, the most active catalysts in radiation catalysis are solids with a wide forbidden gap.

It has been shown in a number of systems that the increase of radiation–catalytic activity with gap width stems from the recombination mechanism for the interaction of a charged adsorbate–hole complex and an electron arriving from the conduction band. Hence a comparison of the forbidden gap with the energy required to break various bonds in the reacting molecule is particularly relevant. This comparison suggests some principles for the selection of radiation–active catalysts.

The study of the nature of catalytically active centres, their structure, the role of free carriers, and the extent to which these take part in the elementary steps of catalytic reactions is greatly assisted by the use of ionising radiation —a powerful agency for altering the concentration electrical charge carriers and for localising carriers on intrinsic defects of the surface.

An analogy has been observed between the active centres formed by conventional methods of catalyst preparation and the active centres of the radiation-induced defect type.

Thus, we may conclude that further developments in the relatively young science of radiation–catalytic processes are vital to the understanding of elementary acts in catalysis.

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Institute of Physical Chemistry
USSR Academy of Sciences, Moscow

U.D.C. 547.593.262

Inositol Phosphatides—Structure, Biochemistry, Synthesis

B.A.Klyashchitskii, S.D.Sokolov, and V.I.Shvets

Progress made during the past 10-12 years in establishing the structure, elucidating the biological role, and synthesising the inositol phosphatides—a class of phospholipids—is discussed. The first part considers problems involved in establishing the structure of mono-, di-, and tri-phosphoinositides, mannosides of phosphatidylinositol, and more complicated "inositide" complexes. The second part deals with the biochemistry of inositol phosphatides, in particular the properties and functions specific to phosphoinositides. The problems and successes in the synthesis of phosphoinositides are discussed in the last part. A large amount of experimental information is used to show the complexity of the selective protection of the hydroxy-groups in myoinositol with the aim of obtaining initial compounds for the synthesis of inositol phosphatides. Work done during recent years is shown to open up a path to the synthesis of optically active phosphoinositides of natural structure. A list of 114 references is included.

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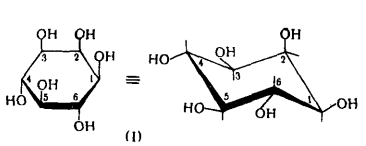
I. INTRODUCTION

The inositol phosphatides are among the most important examples of phospholipids. The presence of phosphoinositides in Nature was first pointed out by Anderson[1], who isolated them from tubercle bacilli. It has now been found that phosphoinositides are present in plants, various animal organs, and micro-organisms: they have been found in soya beans[2], kidney beans[3], milk[4], the brain[5], the liver, kidneys, and other sources[6]. Two reviews have been published dealing in some measure with problems of the structure and synthesis of inositol phosphatides[6,7]. As our knowledge of these compounds becomes deeper and broader, new aspects of their biological role and chemical properties are continually opening up, showing the extraordinary importance of these compounds in the life of various organisms. The present review deals briefly with recent work on the chemistry and the biochemistry of the inositol phosphatides.

II. COMPONENTS AND STRUCTURE OF INOSITOL PHOSPHATIDES

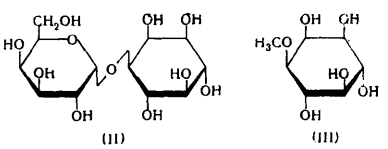
A structural unit of all inositol phosphatides is myoinositol (MI) (I), the only inositol present in Nature in the form of phosphate derivatives[8].



(I)

Myoinositol is widely distributed in Nature, both in the free and in the combined form. It has been found, for example, in rubber latex[9], sperm plasma[10], and sugar beet[11]. It occurs in these sources together with galactin[12], 1-*O*-α-*D*-galactopyranosyl- (1*R*)-myoinositol (II). (Here and subsequently the configuration in asymmetrically substituted derivatives of myoinositol is given in Angyal's notation[13]).

Mention must be made also of such natural myoinositol compounds as (+)-bornesitol[14] or 1-*O*-methyl-(1*R*)-myoinositol (III), α-*D*-galactopyranosyl-(1→6)-α-*D*-galactopyranosyl-(1→1)-myoinositol[15], isolated together with galactin from the roots of the pea, and various myoinositol mannosides, the structure of which will be discussed below.



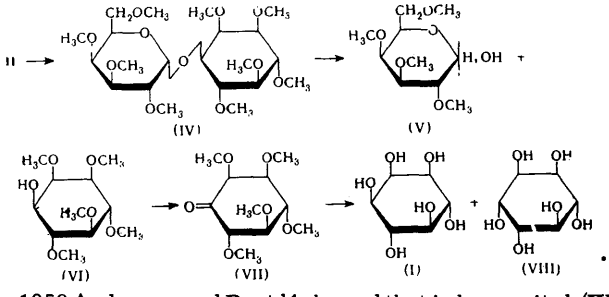
(II) (III)

Sugars and amines must be noted among other components of inositol phosphatides, besides the phosphates, glycerol, and fatty acids usually met in their hydrolysis products. Not long ago many investigators regarded sugars and amines as "impurities" in inositol phosphatides, and endeavoured to remove them by chromatographic and chemical methods of purification[16]. Such "purification" probably resulted frequently in breakdown of the complicated native inositol phosphatide molecule[17]. Anderson[18] showed in several papers that mannose is present in inositol-containing glycolipids of tubercle bacilli. Arabinose and galactose have been found in purified phosphoinositides of soya-beans[19] and lipids of groundnuts[20]. D-Glucose, combined with myoinositol by a glycosidic bond, has been isolated also from the glycolipids of acid-stable bacteria[21]. In 1965 Galanos and Kapoulas worked out a technique for isolating lipid fractions[22], on the basis of which they suggested that lipids, including inositol phosphatides, are present in vegetable and animal tissues as complicated triesters of phosphoric acid[23]. Sugars may also be components of these "triester complexes".

Nitrogen bases also are effective components of inositol phosphatides. Thus aminoethanol has been detected in inositol phosphatides from groundnuts[20], and soya-beans, and in the glycolipid of acid-resistant bacteria. Choline, aminoethanol, and serine may form part of the "triester complexes"[22,23]. Amino-acids—L-ornithine[24], hydroxylysine, asparagine, glutamine, glycine, alamine, etc.—have been observed in many inositol phosphatides[3]. Thus inositol phosphatides containing glutamic and aspartic acids, valine, leucine, threonine, and isoleucine have been isolated from wool fat[25].

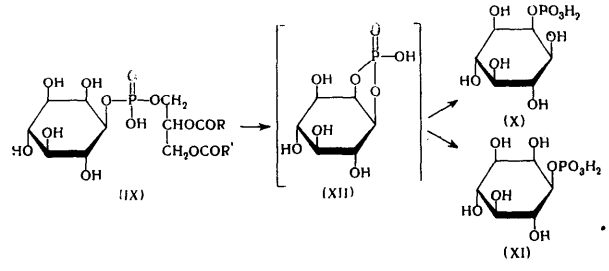
In 1956 the structure of the simplest inositol phosphatides had still not been established; in particular, such an important question as the point of addition of phosphate to myoinositol was obscure[6]. Most workers considered that the phosphate residue was bound to an axial 2-hydroxyl of the myoinositol, since hydrolysis of inositol phosphatides yielded the 2-phosphate.

In 1953 Kabat et al.[12] had established that in galactin (II) a galactopyranose residue was combined by means of an α-glycosidic bond with the 1-hydroxy-group of myoinositol. Methylation of (II) with dimethyl sulphate gave nonamethylgalactin (IV), hydrolysis of which in 0.5 *N* hydrochloric acid yielded 2, 3, 4, 6-tetramethyl-D-galactose (V) and the pentamethyl ether of myoinositol (VI). The latter was oxidised with chromium trioxide to myoinosose (VII), reduction of which followed by demethylation gave both myinositol (I) and (–)-inositol (VIII), which proved the structure given here for galactin (II):



In 1958 Anderson and Post[14] showed that in bornesitol (III) the 1-hydroxy-group of myoinositol had been methylated.

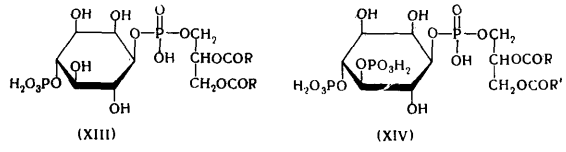
In contrast to these natural compounds of myoinositol, it was very difficult to establish the position of the myoinositol–phosphate bond in phosphoinositides, owing to migration of the phosphate residue during hydrolysis of the natural lipids. The myoinositol molecule (I), having a plane of symmetry through positions 2–5, is optically inactive, but introduction of a substituent into position 1, 3, 4, or 6 should result in the appearance of optical activity. In 1959 several papers were published[26–28] which showed that the hydrolysis of natural phosphoinositides, e.g. phosphatidylinositol (IX), yields a mixture of 2– and 1-phosphates of myoinositol (X) and (XL), which are formed by phosphate migration under conditions of hydrolysis, with intermediate formation of a cyclic ester (XII):



Since the myoinositol 1-phosphate obtained (XI) was optically active, the intermediate cyclic phosphate (XII) should be optically active, which would have been impossible if the myoinositol in the natural compound (X) had been phosphorylated in position 2. This demonstrated that the phosphate residue in natural phosphoinositides is attached to the $C_{(1)}$ atom of the myoinositol molecule.

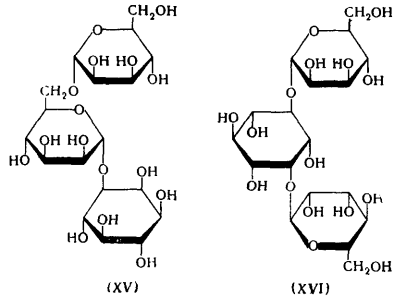
This was confirmed in another paper[27]: glycerylphosphorylinositol, isolated from cow's liver ($[\alpha]_D^{25}$ –13.5° for the cyclohexylammonium salt) yielded after periodate oxidation the optically active glycolaldehydemyoinositol phosphate ($[\alpha]_D^{25}$ –13.2° for the cyclohexylammonium salt: i.e. the main contribution to the optical activity of the natural compound is made by the asymmetrically substituted myoinositol 1-phosphate). Thus in galactin (II), bornesitol (III), and phosphoinositides of soya-beans[29], liver[30], and other sources, myoinositol is substituted in the (equatorial) position 1.

During recent years several major laboratories (those of Ballou, Hawthorne, Dawson, etc.) have been conducting intensive research into polyphosphoinositides possessing great metabolic activity and important biological functions. The structures (XIII) and (XIV) have been established[31–33] for di- and tri-phosphitides:



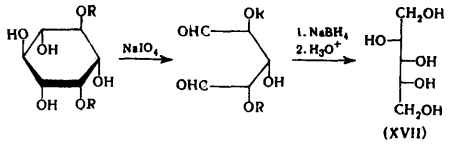
Periodate oxidation of myoinositol triphosphate, isolated from products of the alkaline hydrolysis of the triphosphoinositide of bull's brain, with subsequent reduction and dephosphorylation, gave D-iditol. Similarly, D-threitol was obtained from the diphosphate[32]. From this it was established that the triphosphoinositide was the 4,5-diphosphate of 1-phosphatidyl-(1S)-myoinositol (XIV), and the diphosphoinositide the 4-phosphate of 1-phosphatidyl-(1S)-myoinositol (XIII)[33].

Certain glycolipids of acid-resistant bacteria belong to an interesting class of inositol phosphatides. Anderson showed that these lipids contain a compound of myoinositol with two molecules of mannose, which was termed manninositose[34]. In 1960 Vilkas and Lederer[35] hydrolysed completely methylated manninositose, and obtained an equimolecular mixture of tri- and tetra-*O*-methylmannoses, while periodate oxidation showed the 1→6 bonding of the two mannose residues. On the basis of these results the structure (XV) was assigned to manninositose. This structure was even confirmed by synthesis[36], but in 1964 Lee and Ballou[37], in a brilliant paper on the myoinositol mannosides from the glycolipids of *Mycobacterium tuberculosis* and *Mycobacterium phlei*, showed it to be untenable, and established the structure of manninositose (XVI) and the pentamannoside of phosphatidylmyoinositol.



Exhaustive periodate oxidation of dimannosylmyoinositol with subsequent reduction of the polyaldehydes with sodium tetrahydroborate and acid hydrolysis of the reduction products yielded arabitol (XVII) (the D-configuration was established for (XVII) in the case of the pentamannoside of

myoinositol) and glycerol (from carbon atoms 4, 5, and 6 of the mannoses) in the proportions 1 : 2:

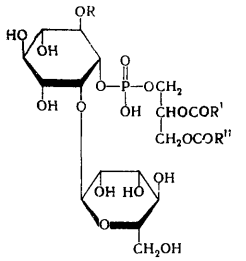


(XVII)

Exhaustive methylation of the dimannoside of myoinositol followed by methanolysis led to the formation of two moles of 2, 3, 4, 6-tetra-*O*-methylmannose per mole of 1, 3, 4, 5-tetra-*O*-methylmyoinositol. The structure of the latter was confirmed also by the nuclear magnetic resonance spectra. The α-glycosidic bonds in the dimannoside of myoinositol were established from the signal of the anomeric proton in the n.m.r. spectrum of this compound.

The phosphatidic acid residue in mannosides of phosphatidylmyoinositol should be present in position 1 of the myoinositol ring, since only this can explain the formation on periodate oxidation from the same products as in the oxidation of myoinositol dimannoside. Thus the glycolipid from *Mycobacterium tuberculosis* is 1-phosphatidyl-2, 6-di-*O*-α-D-mannopyranosyl-(1S)-myoinositol (XVIII)[37]. The presence of mannose residues on both sides of the phosphate–myoinositol bond explains the stability of the phosphate diester bridge to alkaline hydrolysis and the unusual stability of intact glycolipids in hot acetic acid (absence of free hydroxyls on the myoinositol ring carbon atoms adjacent to the phosphate bond).

The structure of the myoinositol monamannoside isolated from *Mycobacterium tuberculosis* was proved by exhaustive methylation followed by methanolysis and identification of the resulting pentamethylmyoinositol by comparison with all four possible isomers in gas–liquid chromatography[38]. It was established that the mannose was bound to the 2-hydroxyl of the myoinositol, i.e. that the intact lipid has the structure (XIX):

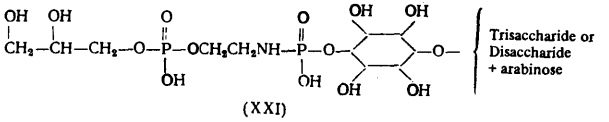


(XVIII: R = α-D-mannopyranosyl); (XIX: R = H); (XX: R = α-D-mannopyranosyl-(1 → 2)-*O*-α-D-mannopyranosyl-(1 → 6)-*O*-α-D-mannopyranosyl-(1 → 6)-*O*-α-D-mannopyranosyl).

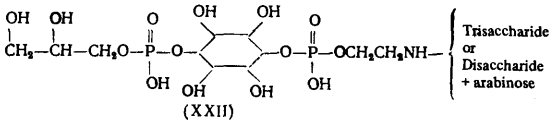
The biosynthesis of phosphatidylmyoinositol dimannoside is probably accomplished by the stepwise glycosylation of phosphatidylmyoinositol, firstly at position 2 and then at position 6 [39].

Complete structures were later established also for the tri-, tetra-, and hexa-mannosides of phosphatidylmyoinositol[40]. Thus the pentamannoside was proved to have the structure 1-phosphatidyl-2-*O*-α-D-mannopyranosyl-6-[*O*-α-D-mannopyranosyl-(1 → 2)-*O*-α-D-mannopyranosyl-(1 → 6)-*O*-α-D-mannopyranosyl-(1 → 6)-*O*-α-D-mannopyranosyl)]-(1S)-myoinositol (XX). Pangborn and McKinney[41] have recently shown that, in the serologically active phosphoinositides of *Mycobacterium tuberculosis*, the ratio of fatty acids to phosphorus is 3 : 1 or 4 : 1; palmitic and tuberculostearic acids were found most frequently among the fatty acids, while little stearic and oleic acids were found. The authors assume that the "excess" acids can be esterified by any free hydroxyls (one or two) in the myoinositol or mannose residues. The same conclusion was reached by Brennan and Ballou[42], who studied the biosynthesis of several mannosylphosphatidylmyoinositols catalysed by intracellular fractions of *Mycobacterium phlei*. They included the three substances which they obtained among the dimannophosphoinositides. The ratio of fatty acids to phosphorus in these compounds was 4 : 1, 3 : 1, and 2 : 1.

Great interest attaches to establishing the structure of the intact complicated lipid complexes which are assumed to be present in animal and plant organisms. One of the first attempts to penetrate the structure of the complicated "inositide complex" was the hypothesis of approximate structures of the inositol phosphatide from groundnuts (XXI and XXII)[6,20]:

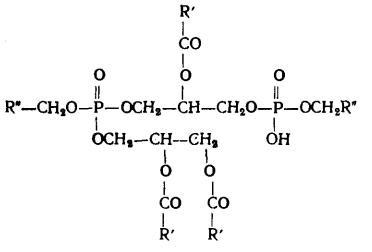


(XXI)

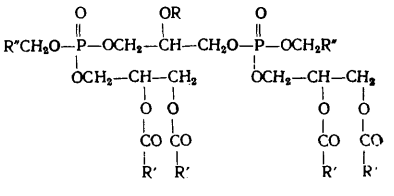


(XXII)

Several authors consider that natural lipid complexes are triesters of phosphoric acid. This view was first expressed by Collins[43], who suggested the possible structures (XXIII) and (XXIV) for such complexes (R = H). Unfortunately, only a few papers have yet been published on the study and structure of lipid "triester complexes". Sinha and Gaby[44] investigated the lipo-amino-acid complexes from *P. aeruginosa*, and regarded these compounds as triesters of phosphoric acid having the structure (XXIV), with R = OCCH(NH$_2$)R‴, the R′ being residues of fatty acids, and R″ residues of nitrogen bases:



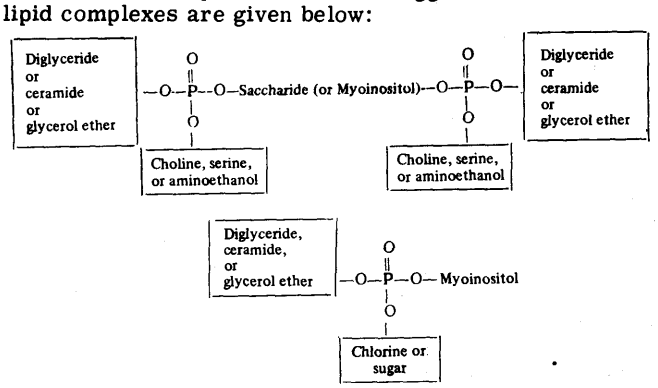
(XXIII)



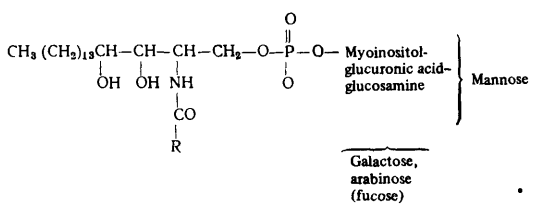
(XXIV)

As already remarked, Galanos and Kapoulas[4,22,23] developed a technique for isolating lipid complexes from natural sources, and proposed several structures for such complexes, in which myoinositol is an important component. They consider that "triester complexes" are actually present in animal and vegetable tissues, while individual phospholipids are merely products of their degradation during isolation from natural sources. These authors note especially the role of myoinositol in stabilising

the "triester complexes". Some suggested structures for lipid complexes are given below:



A series of papers was published by Carter [45] on the isolation from plant seeds of phytoglycolipids containing myoinositol. A study of the degradation products of the phytoglycolipid led to the proposed structure [46]



In 1966 as phingolipid containing dihydrosphingosine, myoinositol, and mannose was isolated from the micro-organisms *Torulopsis utilus* [47].

Further work on the isolation, structure, and synthesis of complicated triester lipid complexes should finally settle the question of their presence in animal and vegetable tissues and their structure.

III. BIOCHEMISTRY OF INOSITOL PHOSPHATIDES

The biochemistry of inositol phosphatides, as members of the class of phospholipids, has been a subject for research in many laboratories, and is quite widely represented in individual papers, reviews, and monographs (e.g. Hawthorne's review [48]). The present Section will survey work done in recent years on properties and functions characteristic of inositol phosphatides.

Phosphoinositides, together with other phospholipids, form structural components of cells. An increased content of inositol phosphatides is found in the cells of certain tissues. Thus the percentage content of inositol phosphatides (and sphingomyelin) in the cells of the lens of the human eye is considerably higher than in other tissues of the body, where lecithin predominates in the phospholipid fraction [49]. It has been suggested that inositol phosphatides have some specific function as structural components of cell membranes in the filaments of the lens of the human eye. Myoinositol labelled with ^{14}C is actively incorporated into the cytoplasmic membranes of the fungus *Neurospora crassa* [50], where it was found that cytoplasmic membranes containing protease were relatively impoverished in lecithin and enriched in inositol phosphatides. Structural integration of protease particles was disturbed in mutants of *N. crassa* grown on a medium containing an insufficient quantity of myoinositol.

Much work has recently been done on the properties of monomolecular films of various phospholipids, which in some measure simulate biological membranes. Studies have been made of the hydrolysis by phospholipase A of monolayers [51] of lecithin, phosphatidyl-aminoethanol, and phosphatidylinositol all labelled with ^{32}P. The change in the surface potential of the film served as a measure of the degree of decomposition of the lipid. Loss of radioactivity by the film on hydrolysis was due to escape of the lyso-compound of the film. Physicochemical and biochemical study of enzymatic hydrolysis in the presence of calcium ions showed the lowest rate of hydrolysis to occur in films of ^{32}P-phosphatidylinositol, which possesses the highest affinity for Ca^{2+}.

Several workers have isolated enzymes specific to inositol phosphatides. Hawthorne [52] isolated from the guinea-pig a phosphoinositideinositolphosphohydrolase which acted on mono-, di-, and tri-phosphoinositides without hydrolysing other phospholipids. Enzymatic hydrolysis yields a diglyceride and inositol phosphates; no inorganic phosphate was detected. English et al. [53] isolated an enzyme termed myoinositolkinase. Myoinositol 1-phosphate was detected among the reaction products.

Inositol phosphatides take part in such important processes in the cell as the change in size of the mitochondria and active transport through the membrane [54]. A "contractile" protein, which was responsible for contraction of the mitochondria on the addition of adenosine triphosphate and magnesium ions, lost its activity on extraction with solvents which remove lipids. The active component was a phosphatidylinositol at a concentration of 10^{-6} M. Other lipids do not possess such activity [55]. In a study of the metabolism of the phosphoinositide complex in the salivary gland of the cat on electrical stimulation, Gaut et al. [56] concluded that increased metabolic activity occurred in the phosphoinositide complex, and they suggested that a phosphoinositide combined with a membrane protein may play an active part in transport processes in the cell. Lipo-amino-acids, in which considerable interest has recently been shown, may also be involved in active transport through the membrane. It is suggested [57], for example, that the synthesis of antibodies involves the formation of a lipo-amino-acid complex on or in the cell membrane, by means of which the amino-acid enters the cell. These complexes may, perhaps, take part in protein synthesis. They may well have the structure of triesters of phosphoric acid [23]. Phosphatidylinositol has been detected in the lipid portion of phosphatidopeptides from lamellae and chloroplasts of the bean. The stability of phosphatidopeptides to acid hydrolysis and their infrared spectra indicate a lipid–peptide ester link [3].

An active part in transport through the membrane is suggested also for the polyphosphoinositides found in various organs and tissues. The metabolism of the phosphoinositide complex of brain was first investigated by Brockerhoff and Ballou [39,58], who showed the path of biosynthesis from monophosphoinositide by phosphorylation to di- and tri-phosphoinositides. Adenosine triphosphate may be the donor of the phosphate group. Later work [59] has confirmed that the incorporation of ^{32}P-orthophosphate into the diphosphoinositide of mitochondrial fractions from the liver is diminished by inhibitors of oxidative phosphorylation. Dephosphorylation takes place together with phosphorylation in the inositide complex, so that a metabolic process is occuccring:

$$\text{Monophosphoinositide} \rightleftharpoons \text{diphosphoinositide} \rightleftharpoons \text{triphosphoinositide}$$

Perhaps this may also explain the biochemical role of the inositide complex in the transport of cations [60].

The extraordinarily high metabolic activity of the inositide complex and its participation in active transport through the membrane have been discussed in many papers during the past three years. Hawthorne[61], studying the place of synthesis of the diphosphoinositides of rat liver, found that they were synthesised mainly in plasmic membranes. He even demonstrated the synthesis of polyphosphoinositides *in vitro* catalysed by a homogenate of rat brain[62]. The high metabolic activity of phosphoinositide complexes is explained by the presence of polyphosphoinositides in them. Freyss et al[63] showed a high rate of metabolism of inositol phosphatides compared with other phospholipids, when studying the metabolism of various phospholipids in the brain of the rat, and Nicolas[64] reached the same conclusion, having established a more rapid loss of radioactivity by the inositol phosphatides of myelin labelled with 1-^{14}C-acetate, compared with cerebrosides, phosphatidyl-aminoethanol, and other lipids.

The biochemistry of other inositol phosphatides is also unusual. Inositol monophosphatides containing residues of two different fatty acids, isolated from the lipid fractions of horse brain, are found[65] to be blood anticoagulants. Bacterial glycolipids possess serological activity. Phosphatide antigens of several mycobacteria have been identified as mannosides of phosphatidylinositol[66]. They fix complement in a serum containing antibodies against tubercle bacilli. The glycolipids of acid-stable bacteria are very toxic: an adult mouse is killed 5–8 days after the injection of 5–10 μg. The cause of death is not yet clear. The injection of certain lipid fractions of tubercle bacilli produces immunisation of animals, increasing, for example, the lifetime of a mouse which has been inoculated with virulent tubercle bacilli. Detailed information on the biological role and functions of the glycolipids of acid-resistant bacteria will be found in Lederer's review[67].

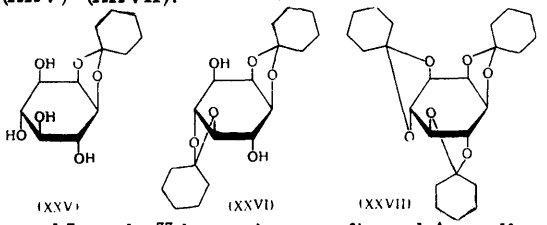
Many papers have been published also on the biosynthesis and the metabolism of myoinositol[68-70]. It has been established that myoinositol plays a part in cellular morphogenesis, lipid synthesis and transport, the transport of ions and hormones through cell membranes, and other important vital processes[71]. A detailed account of the biochemistry of myoinositol has been given in a recent review by Posternak[72].

IV. SYNTHESIS OF INOSITOL PHOSPHATIDES

Besides a biochemical study, many laboratories are occupied with synthetic investigations on the inositol phosphatides. Phosphoinositides themselves—in particular their main component, myoinositol—provide a wide field of activity for organic chemists. The urgent requirements of biochemistry and biology also lead to synthetic investigations on phospholipids. For example, Collins[43] regards the synthesis of triesters of phosphoric acid, the structure which he suggested, as having great value in confirming their presence in Nature and in studying their properties. In fact, the isolation of such labile substances from natural sources requires colossal amounts of labour, and ultimately does not yield quantities sufficient for a systematic study of their properties and biological activity. A similar opinion is held by Ballou[37,38].

A comprehensive study of the chemistry of myoinositol is being made in Angyal's laboratory. This work is of great value for the synthesis of inositol phosphatides. The myoinositol molecule (I) contains six hydroxyls, five of which are equatorial, while one, in position 2, is axial. The myoinositol molecules have the chair form, as has been confirmed by X-ray examination[73]. This structure creates fundamental difficulties in the synthesis of inositol phosphatides in which myoinositol is combined with phosphate in position 1. Various protective groups for the hydroxyls have been studied, but until recently none of them has enabled a protected myoinositol to be prepared with a free 1-hydroxyl, a key intermediate in the synthesis of inositol phosphatides. Isopropylidene protection was used in the early work, and with its help methyl ethers of myoinositol were synthesised in low yields[74].

Subsequently cyclohexylidene derivatives of myoinositol, prepared in good yield by reaction with cyclohexanone, have come to be employed. Angyal[75,76] has prepared mono-, di-, and tri-cyclohexylidene derivatives of myoinositol (XXV)–(XXVII):

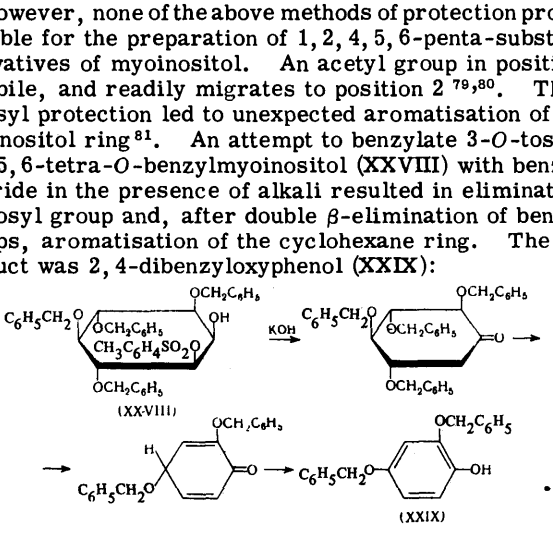


(XXV) (XXVI) (XXVII)

Mager and Ionesku[77] have since confirmed Angyal's observation that acetals are first formed at *cis*-hydroxyls (*ae*), and only then at *trans*-hydroxyls (*ee*). Angyal and Tate[78] have synthesised myoinositol 4- and 5-monophosphates and 1,4-, and 1,6-, and 4,5-diphosphates from cyclohexylidene derivatives of myoinositol.

Further efforts were directed at the selective protection of the 2-hydroxy-group in 1,4,5,6-tetra-substituted derivatives of myoinositol, which are easily obtained from 1,2-cyclohexylidenemyoinositol (XXV). It was shown that several substituents occupy the 3-equatorial position preferentially, whereas others do not display such selectivity. Thus the acetylation[79], tosylation[80], benzylation, and methylation[81] of the tetra-substituted derivatives take place selectively at position 3, whereas tetrahydropyranyl protection is not selective[82]. It was suggested[81] that reactions involving a transition state (etherification, substitution by an S_N2 mechanism) take place preferentially at position 3 owing to great steric hindrance at position 2. Rapid reactions (substitution by an S_N1 mechanism) are less sensitive to steric hindrance, and therefore occur non-selectively.

However, none of the above methods of protection proved suitable for the preparation of 1,2,4,5,6-penta-substituted derivatives of myoinositol. An acetyl group in position 3 is labile, and readily migrates to position 2[79,80]. The use of tosyl protection led to unexpected aromatisation of the myoinositol ring[81]. An attempt to benzylate 3-*O*-tosyl-1,4,5,6-tetra-*O*-benzylmyoinositol (XXVIII) with benzyl chloride in the presence of alkali resulted in elimination of the tosyl group and, after double β-elimination of benzyl groups, aromatisation of the cyclohexane ring. The final product was 2,4-dibenzyloxyphenol (XXIX):

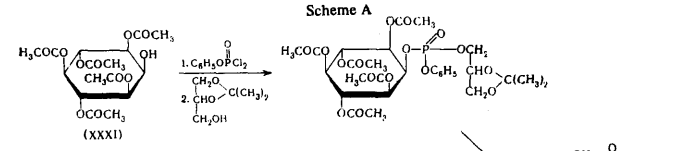


(XXVIII) (XXIX)

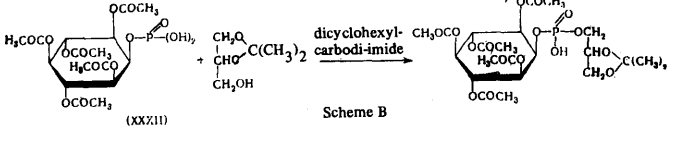
In 1966 the preparation was reported of DL-1,2,4,5,6-penta-*O*-benzylmyoinositol[83], which serves as a convenient intermediate for the synthesis of racemic inositol phosphatides. In this synthesis Gigg used allyl protection, previously employed in the chemistry of carbohydrates[84]. Allyl protection was introduced selectively in position 3 of 1,4,5,6-tetra-*O*-benzylmyoinositol, the product was then benzylated at position 2, and after isomerisation of the allyl group into propenyl the latter was removed by acid hydrolysis. Finally, Angyal[85] has recently shown that 1-benzyl-2,3,4,5,6-penta-acetylmyoinositol can be obtained by the acetolysis of 1,4,5,6-tetrabenzylmyoinositol, owing to steric hindrance to acetolysis of the benzyl group at position 1. Hydrogenolysis of the product yielded 1,2,4,5,6-penta-acetylmyoinositol. All this work shows how complicated and interesting is the problem of the selective protection of the hydroxy-groups in myoinositol.

The first synthesis of a product of the hydrolysis of inositol phosphatides—myoinositol 2-monophosphate—was accomplished in 1949 by Iselin[86], by the reduction of scyllo-mesoinosose penta-acetate with subsequent phosphorylation with diphenyl phosphorochloridate and removal of the protective groups. As already remarked in Section II, it was thought at that time that the phosphate in inositol phosphatides was attached to the $C_{(2)}$ atom of the myoinositol molecule. Only after ten years did Davies and Malkin[87] and at the same time Ellis and Hawthorne[88] synthesise 1-glyceryl-2-myoinositol phosphate (XXX) by different methods: the former by the reaction of 1,3,4,5,6-penta-*O*-acetylmyoinositol (XXXI) with phenyl phosphorodichloridate and 1,2-isopropylideneglycerol (Scheme A); and the latter by condensing (XXXII), the 2-phosphate of (XXXI), with 1,2-isopropylideneglycerol in the presence of dicyclohexylcarbodi-imide (Scheme B).

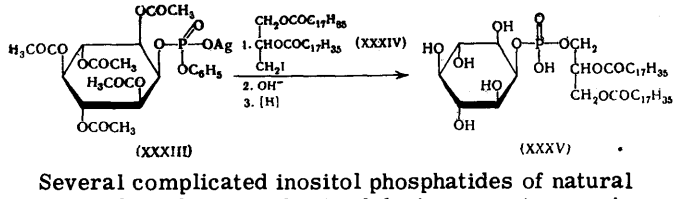
Scheme A



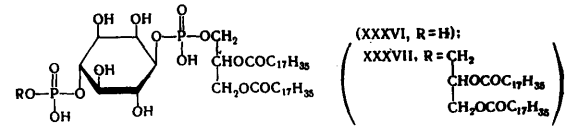
Scheme B



Davies and Malkin[89] also obtained the inositol phosphatide (XXXV) by condensing the silver salt of a protected 2-phosphate of myoinositol (XXXIII) with the iodide of 1,2-distearoylglycerol (XXXIV), but it subsequently became clear that the product did not have the natural structure:

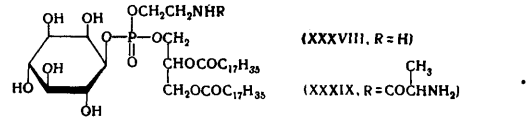


Several complicated inositol phosphatides of natural structure have been synthesised during recent years in Preobrazhenskii's laboratory. Thus Preobrazhenskii, Shvets, et al.[90] prepared the 1,4-diphosphoinositides (XXXVI) and (XXXVII) by condensing 1,2:4,5-dicyclohexylidenemyoinositol (XXVI) with phosphoryl chloride and 1,2-distearoylglycerol:



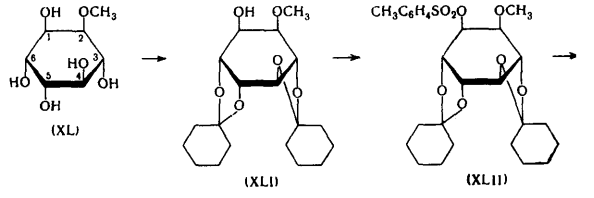
These compounds may be fragments of more complicated lipid complexes.

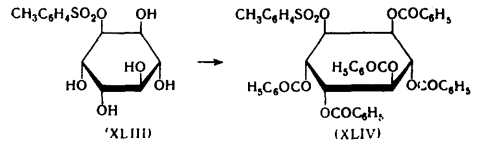
The same workers[91] were the first to obtain inositol phosphatides having the structure of triesters of phosphoric acid (XXXVIII), and simulating a possible bond between the lipid and the amino-acid moieties in lipo-amino-compounds (XXXIX):



Unfortunately, all the inositol phosphatides described were isolated in the optically inactive, racemic form. In natural phosphoinositides the myoinositol molecule is asymmetrically substituted in the equatorial 1-position, and hence possesses optical activity. This has been demonstrated both for simple inositol phosphatides[26-30] and for the complicated complexes. It has been established[92], for example, that brain triphosphoinositide has the structure 2,3-di-*O*-acylglyceryl-1-[(1′*S*)-myoinositol 1′,4′,5′-triphosphate].

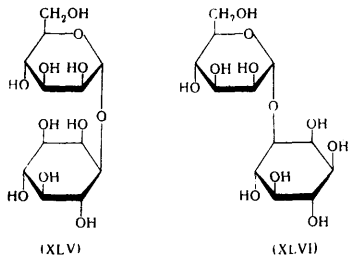
In practice the problem of synthesising optically active inositol phosphatides has still not been solved. It is true that Ballou[29] reported in 1959 the synthesis of optically active myoinositol 1-phosphate, which can serve as intermediate for the synthesis of optically active inositol phosphatides. The starting material in this synthesis was galactin (II), which was completely benzylated by Kuhn's method; methanolysis with 1% hydrochloric acid led to cleavage of the α-glycosidic bond in nonabenzylgalactin, the resulting 1,2,4,5,6-penta-*O*-benzylmyoinositol was phosphorylated with diphenyl phosphorochloridate in the free 3-position, and after removal of protective groups the optically active myoinositol 1-phosphate was obtained[93]. Gero[94] has recently suggested a different route to this optically active compound, starting from quebrachitol, 2-*O*-methyl-(−)-inositol (XL). 3,4:5,6-Di-*O*-cyclohexylidenequebrachitol (XLI) was obtained[73] from (XL), and then converted into 3,4:5,6-di-*O*-cyclohexylidene-2-*O*-methyl-1-*O*-tosyl-(−)-inositol (XLII). After elimination of the methyl group with boron trichloride in dichloromethane at −80°C the unstable 1-*O*-(−)-inositol (XLIII) was obtained. This was benzoylated, and optically active myoinositol 1-phosphate could be obtained from the final products, 2,3,4,5,6-penta-*O*-benzoyl-1-*O*-tosyl-(−)-inositol (XLIV), after removal of the tosyl group, inversion of the 1-hydroxyl, and phosphorylation:





(XLIII) (XLIV)

However, optically active naturally occurring compounds—galactin and quebrachitol—were used as starting materials in these syntheses[93,94]. Purely chemical methods of obtaining optically active 1-*O*-substituted myoinositols have not yet been developed because of the great difficulty of separating the resulting racemic mixtures into optical isomers. The only example of such a separation is the work of Angyal and Shelton[95] on the synthesis of 1-*O*-α-D-mannopyranosylmyoinositols—(XLV) and (XLVI)—and α-D-mannopyranosyl-(1→6)-*O*-α-D-mannopyranosyl-(1→1)-myoinositol (XV). Mannosylmyoinositol was obtained by the Königs-Knorr reaction from 1,4,5,6-tetra-*O*-acetylmyoinositol and tri-*O*-acetyl-α-D-mannopyranosyl bromide, the low yield (4.5%) being explained by large steric hindrance. Mannosylmyoinositol is easily separated into two diastereomers—1*S* (XLV) and 1*R* (XLVI)



(XLV) (XLVI)

These diastereomers could have served as starting material for the preparation of optically active 1-*O*-substituted derivatives of myoinositol, but the low yield gives no grounds for regarding this work as a practical route to optically active phosphoinositides. The same workers[95] synthesised galactin in 2.1% yield by the Königs-Knorr reaction. In this case the diastereomers were separated by seeding with crystals of natural galactin.

During recent years great successes have been achieved in studying the chemistry and the biochemistry of inositol phosphatides. The structure of several "inositide complexes" has been elucidated, and methods have been developed for isolating them from vegetable and animal tissues. Inositol phosphatides undoubtedly play an important part in the most intimate processes in the cell. But the structure of many complicated phosphoinositides, their complexes with amino-acids and proteins, and the biological role of such compounds have hitherto formed subjects of hypothetical assumptions. Although there are considerable achievements in the chemistry of inositol phosphatides, in the synthesis of complicated lipid complexes simulating possible natural structures, the problem of preparing optically active phosphoinositides, which are of the greatest interest for biology, is still unsolved. The synthesis of these compounds will probably be accomplished in the near future.

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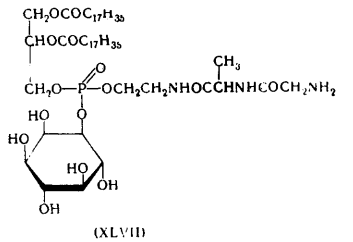
Many papers on the structure, biochemistry, and synthesis of inositol phosphatides have been published while the manuscript was being prepared for press.

Scamark et al.[96] have shown for the first time that 1-*O*-(D-glycerylphosphoryl)-(1*S*)-myoinositol is present as a normal component in biological tissues, not as a degradation of complicated phosphoinositides. They isolated this compound from the prostate gland and the epididymis of rats, and from bull and ram semen. Di- and tri-phosphoinositides have been isolated from baking yeast (*Saccharomyces cerevisiae*)[97].

The detection of mannophosphoinositides in various species of bacteria indicates the close phylogenetic and taxonomic relations of these species. Mannophosphoinositides have been isolated from *Propionibacterium shermanii*[98], *Streptomyces sioyaensis*[99], *Corynebacterium xerosis*[100], and others[101,102]. Ballou and Brennan[103] have continued to study the biosynthesis of mannophospjoinositides of *Mycobacterium phlei*. The enzymatic acylation of dimannophosphoinositides is discussed in the same paper. The high metabolic activity of phosphoinositides is confirmed in several papers. A tracer is incorporated into the phosphatidylinositol in *Nocardia polychromogenes* eight times as rapidly as into a cardiolipin[104]. Nakatani et al.[105] have investigated the incorporation of inorganic phosphate *in vitro*. Phosphorus-32 is incorporated more rapidly into phosphatidylinositol than into lecithin (in the coronary artery of the bull, for example, by factors of 4.9–5.3). It has been shown[106] that acetylcholine stimulates cleavage of the phosphodiester bond in the phosphoinositides of the guinea-pig brain. Enzymes specific to phosphoinositides continue to be studied. Thus Lee and Huggins have reported on the structure[107], purification, and properties[108] of triphosphoinositidephosphomonoesterases from rat kidneys. The role of phosphoinositides and complicated inositide complexes in organising the membranes of the nervous system is discussed from the point of view of evolution in Kreps's book[109].

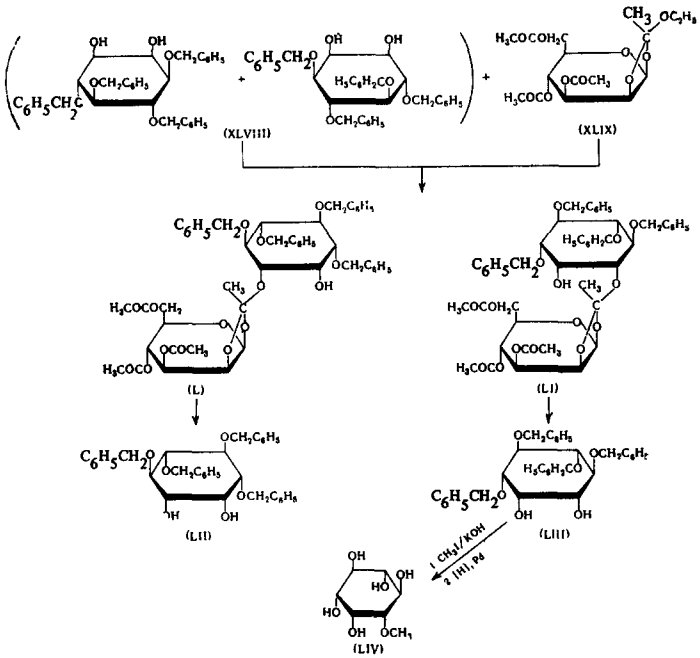
N. A. Preobrazhenskii's school enjoys a leading position in synthetic investigations on the inositol phosphatides. In 1968 Preobrazhenskii, Zhdanovich, Lyutik, et. al.[110] synthesised *O*-[α-(α′β-distearoyl)glycerylphosphoryl-(1-myoinositol)]-*N*′-(glycylalanyl)amino-ethanol (XLVII), the simplest phosphatidopeptide, which is a model of possible structures for the phosphatidopeptide fractions from tissues of brain, liver, etc. The same workers[111] have reported the synthesis of a monophosphoinositide containing the phosphatidyl residue in position 1, the starting material being 1,2,4,5,6-penta-*O*-acetylmyoinositol[85]. Preobrazhenskii, Tarusova, Kozlova, et al. have investigated[112] the benzoylation of 1,2 : 4,5-dicyclohexylidenemyoinositol (XXVI), and have shown that position 3 in the myoinositol is benzoylated preferentially.



(XLVII)

Continuing his previous work[94] aimed at obtaining optically active phosphoinositides, Géro[113] has synthesised 1,2,4,5,6-penta-*O*-benzoyl-(1*S*)-myoinositol, using quebrachitol as starting material. Unfortunately, the optical isomer which he has obtained does not yield phosphoinositides of natural structure, in which the phosphatidyl residue is bound[26-30] to the (1*S*)-position in myoinositol.

Preobrazhenskii and the present Reviewers [114] have recently developed a method for separating racemic asymmetrically substituted myoinositols via diastereomeric orthoesters with carbohydrates, which enables both optically active isomers to be isolated in optically pure form. 1,4,5,6-Tetra-*O*-benzylmyoinositol (XLVIII) was subjected to transesterification with 3,4,6-tri-*O*-acetyl-1,2-*O*-ethylorthoacetyl-β-D-mannopyranose (XLIX), the resulting diastereomeric orthoesters (L) and (LI) were separated by crystallisation and chromatography, and 1,4,5,6-tetra-*O*-benzyl-(1*S*)-myoinositol (LII) and its (1*R*)-enantiomer (LIII) were isolated from the separated orthoesters (L) and (LI) by mild acid hydrolysis. The first complete synthesis of (−)-bornesitol (LIV) has been accomplished from the (1*R*)-enantiomer.



The possibility of separating various asymmetrically substituted myoinositols into enatiomers opens up a path to the synthesis of optically active phosphoinositides of natural structure.

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Lomonosov Moscow Institute of Fine Chemical Technology

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Complexes of Molecular Nitrogen

Yu.G.Borod'ko and A.E.Shilov

The review deals with problems associated with the formation and structure of complexes of molecular nitrogen with transition metal compounds, metals, and other active species. Nitrogen interacts very weakly with acceptors of the type BF_3 but is capable of forming more stable systems (of the type of diazo-compounds) with species having both acceptor and donor properties (CH_2, CH, O).

On the surface of metals (nickel, palladium, platinum), nitrogen forms complexes with the linear configuration of the fragment M-N≡N.

A large number of stable complexes (nitrogenyls), also with a linear configuration of the M-N≡N fragment and analogous to the carbonyls and diazo-compounds, have been obtained recently with compounds of iron(II), ruthenium(II), osmium(II), cobalt(I), rhodium(I), iridium(I), and nickel(0). In addition, dinitrogenyl compounds $L_n M(N_2)_2$ and dinuclear complexes M-N≡N-M are known.

In nitrogenyl compounds nitrogen behaves as a π-electron acceptor ligand and therefore donor ligands stabilise the $M-N_2$ bond in the complex and acceptor ligands weaken it.

The method of synthesis of nitrogenyl complexes, their properties, and the mechanism of their formation have been examined. The possibility of the involvement of dinuclear complexes in nitrogen fixation under mild conditions is discussed.

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I. INTRODUCTION

In the last three years the chemistry of a new class of coordination compounds, complexes of molecular nitrogen with transition metal compounds, has arisen and has been developing vigorously. Although the first such complex was synthesised as late as 1965, at the present time dozens of similar compounds are known and some of them are surprisingly stable. By analogy with the carbonyls, it has been suggested that they be called nitrogenyl complexes.

It is noteworthy that, even before the preparation of these complexes, hypotheses were put forward concerning the possibility of the coordination of molecular nitrogen and the probable structure of the complexes. The great interest in the complexes of molecular nitrogen is due to the fact that they are probably intermediates in reactions involving the binding of molecular nitrogen, in particular in biological nitrogen fixation. Chemisorption and hydrogenation of nitrogen on the surface of various metals are closely associated with the formation of the complexes.

Studies in recent years have shown that molecular nitrogen is capable of interacting not only with transition metals and their compounds but also with a number of other active species in the gas phase and in solution, the reactions being to a considerable degree related. Therefore such investigations are also included in the review.

The range of studies involving the formation of the complexes and reactions of molecular nitrogen under mild conditions has been rapidly developing recently and it is likely that new reviews will be necessary in the near future.

II. PHYSICOCHEMICAL PROPERTIES OF MOLECULAR NITROGEN

Table 1 lists certain physicochemical characteristics of molecular nitrogen. It is readily seen that the nitrogen molecule has very high dissociation energies and ionisation potentials and exhibits an appreciable quadrupole moment and polarisability.

Table 1. Physicochemical properties of molecular nitrogen

Interatomic distance r_e	1.0975 Å
Quadrupole moment	-1.4×10^{-26}
Anisotropy of the polarisability ($\alpha_{\parallel} - \alpha_{\perp}$)	0.696×10^{-24} cm^3
Ionisation potential	367 kcal mole^{-1}
Electron excitation energy	
$^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$	142 kcal mole^{-1}
$^1\Sigma_g^+ \rightarrow \Pi_g$	196 kcal mole^{-1}
Dissociation energy ($^1\Sigma_g^+$)	225 kcal mole^{-1}
Vibration frequency (gas)	2331 cm^{-1}
Anharmonicity constant	0.006
Rotational constant	1.9983
Solubility:	
in water (20°C)	1.7×10^{-2} cm^3 cm^{-3}
in benzene (20°)	1.11×10^{-1} cm^3 cm^{-3}

The inertness of molecular nitrogen is attributed to the high stability of the first bond to be dissociated in the N_2 molecule. The energy of this bond amounts to about 130 kcal mole^{-1},[1] which greatly exceeds the corresponding values for other multiple bonds. For example, in acetylene the dissociation of the first bond requires only 53 kcal mole^{-1}.[1] Pauling[1] explains the deviation from linearity of the variation of the dissociation energy of the nitrogen–nitrogen bond with increasing bond order (Fig. 1) by the lower repulsion energy of the unshared electron pair in molecular nitrogen compared with the N=N and N–N bonds.

The positions of the upper filled and lower unfilled molecular levels of the interacting molecules play a significant role in the formation of the complexes, since they determine the donor–acceptor properties of the interacting species.

Let us now consider the system of molecular orbitals of the N_2 molecule. Eight molecular orbitals are formed from the eight sp^3 orbitals of the two nitrogen atoms. The sequence of the filled molecular orbitals of the nitrogen molecule ($^1\Sigma_g^+$) with increasing energy (Fig. 2) is as follows: $1\sigma_g^2$, $1\sigma_u^2$, $2\sigma_g^2$, $2\sigma_u^2$, $1\pi_u^4$, and $3\sigma_g^2$. The highest filled level is the bonding $3\sigma_g$ level, since ionisation of N_2 results in the formation of the N_2^+ ion ($^2\Sigma_g^+$) by removal of a $3\sigma_g$ electron[2,3]. It is noteworthy that, in contrast to N_2, the upper filled 3σ level of carbon monoxide is of the non-bonding type[4] and this is precisely the reason for the significant difference between N_2 and CO as ligands in complex formation (see pp. 360 and 367).

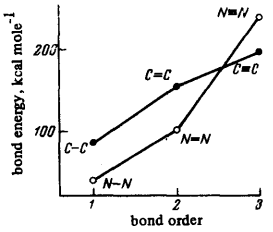


Figure 1. Dependence of the energy of the nitrogen–nitrogen and carbon–carbon bonds on bond multiplicity.

The removal of electrons from bonding orbitals weakens the nitrogen–nitrogen bond while their removal from antibonding orbitals strengthens the bond. In diatomic molecules this affects the interatomic distances and frequencies of the stretching vibrations.

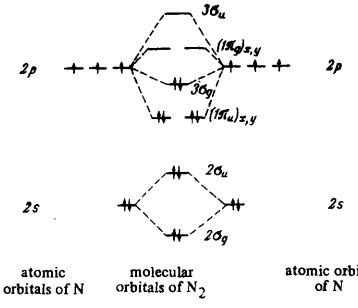


Figure 2. Molecular orbitals of N_2 (arbitrary scale).

The ionisation potentials, interatomic distances, and vibration frequencies (Table 2) confirm the sequence of molecular orbitals presented in Fig. 1. The removal of an electron from the strongly antibonding $2\sigma_u$ level leads to a decrease in the interatomic distance and an increase in the vibration frequency, while the removal of $3\sigma_g$ and $1\pi_u$ electrons greatly weakens the N≡N bond. The $3\sigma_g$, $1\pi_u$, and $2\sigma_u$ molecular orbitals of nitrogen are located relatively close to one another and small changes in interatomic distance can alter the sequence of these levels[5].

The ionisation potential of N_2 is 360 kcal mole^{-1}† and the dissociation energy of N_2^+ remains fairly high (201 kcal mole^{-1}). The electron affinity of molecular nitrogen, which characterises the position of the lower unfilled level,

† All the energy values quoted in the review without a reference were taken from Ref. 9.

is important. In this connection studies[6,7] on the scattering of slow electrons by molecular nitrogen, which showed that electrons with energies of 53 kcal mole^{-1} collide inelastically with N_2, are of interest. The observed low-energy resonance is probably associated with the excitation of the short-lived virtual negative ion N_2^- ($^2\Pi_g$), the potential energy minimum of which is higher by 34 kcal mole^{-1} than the lowest vibrational state of N_2($^1\Sigma_g^+$).[8] These data lead to the conclusion that in the excited state N_2 possesses considerable electron affinity.

Table 2. Physical constants of N_2 in various electronic states*

	N_2			N_2^+		
	$^1\Sigma_g^+$	$^3\Sigma_u^+$	$^1\Pi_g$	$^2\Sigma_g$	$^2\Pi_u$	$^2\Sigma_u^+$
Interatomic distance r, Å	1.09			1.12	1.17	1.07
Vibration frequency ν_e, cm^{-1}	2358			2207	1902	2419
Dissociation energy D_e, kcal mole^{-1}	225	83	138	201		
Ionisation potential of the N_2 molecule ($^1\Sigma_g^+$), kcal mole^{-1}	360 ($3\sigma_g$); 390 ($1\Pi_u$); 430 ($2\sigma_u$)					

* The interatomic distances and the vibration frequencies have been taken from Ref. 5 and the ionisation potentials from Ref. 3.

We may note that in carbon monoxide, which is isoelectronic with respect to nitrogen, resonance is observed at an electron energy of about 39 kcal mole^{-1}. The dissociation energy of "hot" nitrogen molecules in long-lived states is greatly reduced (Table 2).

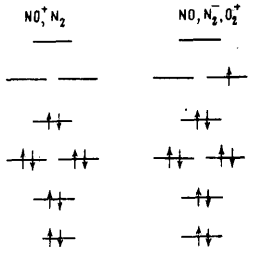


Figure 3. The system of molecular orbitals of NO^+ and N_2 and of NO, N_2^-, and O_2^{2+} (arbitrary scale).

In order to obtain some idea about the weakening of the nitrogen–nitrogen triple bond in the N_2^- ion, we shall compare the dissociation energies of the isoelectronic molecules NO^+ and N_2, and also NO, N_2^-, and O_2^+ (Fig. 3). The dissociation energy of NO^+ is 252 kcal mole^{-1}. The introduction of an electron into the antibonding $1\pi_g$ orbital reduces the strength of the nitrogen–oxygen bond and the dissociation energy of NO is 152 kcal mole^{-1}. The dissociation energy of the O_2^+ molecule, isoelectronic with NO and N_2^-, is 153.5 kcal mole^{-1}. Assuming that in the transition from N_2 to N_2^- the dissociation energy diminishes in proportion to the energy change on going from NO^+ to NO, we obtain about 140 kcal mole^{-1} for the dissociation energy of the N_2^- ion. On the basis of this value, it is possible to estimate the electron affinity (EA) of N_2 from the following cycle:

$$\begin{aligned} &N_2 + e \rightarrow N_2^- && +EA,\\ &N_2^- \rightarrow N^- + N && -140 \text{ kcal mole}^{-1},\\ &N^- \rightarrow N + e && -1 \text{ kcal mole}^{-1},\\ &N + N \rightarrow N_2 && +225 \text{ kcal mole}^{-1},\\ &\overline{EA = -84 \text{ kcal mole}^{-1}}. \end{aligned}$$

Thus, in accordance with this estimate, the affinity of the nitrogen molecule for an electron is a large negative quantity. The electron affinity obtained and the ionisation potential of the N_2 molecule show that the ionic states N_2^+ and N_2^- are difficult to achieve on energetic grounds, i.e. reactions with complete electron transfer

$$N_2 + D \rightarrow N_2^- + D^+$$
$$N_2 + A \rightarrow N_2^+ + A^-$$

are very unlikely (here D is an electron donor and A an acceptor).

III. REACTIONS OF N_2 WITH NON-METAL DERIVATIVES

Several examples of non-elastic collisions of N_2 with the molecules of other gases are known at present.

1. Collision Complexes in the Gas Phase

In a mixture with carbon dioxide, H_2, and other gases under a pressure of several tens of atmospheres, nitrogen absorbs infrared radiation. Then the spectrum of the gaseous mixture shows both the frequency corresponding to the fundamental vibration of N_2 and the sum and difference frequencies with the colliding molecules. Such vibrational transitions are due to the simultaneous excitation of the two interacting molecules by a single light quantum[10].

In an inelastic collision the electrical charges of the molecules are redistributed, as a result of which vibration frequencies corresponding to forbidden transitions appear in the infrared spectrum. Thus Fahrenfort and Ketelaar[11] observed absorption bands at 2331, 2995, and 4670 cm^{-1} in the spectrum of a mixture of N_2 with CO_2. The last two are combination frequencies:

$$\nu(N_2) + \nu'(CO_2) = 2331 + 2349 = 4680 \text{ cm}^{-1},$$
$$\nu(N_2) + \nu''(CO_2) = 2331 + 667 = 2998 \text{ cm}^{-1}.$$

It has been shown experimentally that the intensity of infrared absorption corresponding to simultaneous transition in a complex of two molecules is proportional to the pressures of both mixture components, i.e. the transitions occur in bimolecular collisions.

Under normal conditions, the lifetime of collision complexes should not exceed 10^{-13} s, since the interaction energy of the components of the complex is very low.

2. Interaction of Molecular Nitrogen with Water, Hydrogen Chloride, and Boron Trifluoride

Van der Waals forces play a significant role in the formation of "collision complexes" of molecular nitrogen. However, it has been shown[12] that the formation of complexes as a result of exchange interactions, similar to hydrogen bonding, is possible. In the study of the broadening

of the rotational lines of the R- and P-branches of the rotational vibrational bands of water, hydrogen chloride, and methane in a mixture with different gases, it was found[12] that the effect of the gases in the broadening of the water and hydrogen chloride lines increases in the sequence He, Ar, O_2, and N_2. N_2 is almost twice as effective as argon, although the effect of argon and nitrogen on the methane molecule is almost the same (Table 3).

Table 3. Collisional broadening cross-sections (10^{-16} cm^2) of molecules[12] with Ar and N_2

Molecule	λ, nm	Ar	N_2
H_2O	1.45	41 (30) *	85 (32)
HCl	1.7	62 (50)	116 (53)
CH_4	1.7	50 (28)	50 (30)

* The gas-kinetic cross sections are indicated in brackets.

The difference in the broadening effects of argon and molecular nitrogen on the rotational lines of water and hydrogen chloride has been attributed to the formation of the hydrogen bonds N_2...HCl and N_2...HOH.

In order to investigate the donor–acceptor interaction of nitrogen with powerful acceptors, the infrared spectra of mixtures of nitrogen with boron trifluoride were investigated[13]. A change in the contour and integral intensities of the $\nu_2(A'')$ and $\nu_3(E)$ bands of boron trifluoride, corresponding to an increase in the moment of inertia and the dipole moment of the B–F bond in the BF_3 molecule, were observed.

Table 4. Electro-optical parameters $\partial\mu/\partial Q$ and the dipole moments μ_{B-F} of boron trifluoride mixed with various gases[13]

Gas	$\partial\mu/\partial Q$, CGSU/cm^{-1} g$^{-1/2}$	$10^{18}\mu_{B-F}$, CGSE
BF_3 *	101.5	1.7
BF_3+He **	103	1.75
BF_3+H_2 (D_2)	104.5	1.77
BF_3+Ar	111	1.9
BF_3+N_2	116.5	2.0

* The pressure of BF_3 was in all cases 20–30 mmHg.
** The pressure of the gas interacting with BF_3 was 70 atm.

Compared with other gases (helium, hydrogen, deuterium, and argon), nitrogen has the greatest effect on the integral intensity and the dipole moment of the B–F bond; argon is the next most effective gas in this respect (Table 4).

The increase of the moment of inertia and of the polarity of the B–F bond in mixtures of boron trifluoride with argon and nitrogen is evidence of the formation of donor–acceptor molecular complexes in which N_2 behaves as an electron donor by virtue of its unshared electron pair or the π electrons of the triple bond and BF_3 behaves as an acceptor by virtue of the unfilled $2p_z$ orbital of boron. The complexes of boron trifluoride with argon were known even earlier[14].

It is noteworthy that the intensities $\mathcal{I}\nu_2$ and $\mathcal{I}\nu_3$ vary little in the nitrogen pressure range 1–70 atm and therefore a very low concentration of the complexes is formed even at high pressures.

Evidently, by itself donor–acceptor interaction, even with powerful acceptors such as boron trifluoride, leads to the formation of complexes with only a very weak bond, i.e. nitrogen may be regarded as a very weak base.

So far there is no information about the structure of the unstable donor–acceptor complexes of molecular nitrogen in the gas phase.

3. Interaction of Nitrogen with Carbenes and Related Species

Organic diazo-compounds and diazonium salts may be arbitrarily regarded as complexes of molecular nitrogen with carbenes and aryl cations respectively[15]. Nitrous oxide (N_2O) and hydrazoic acid (HN_3) may be included among these compounds. In fact the interatomic distance r_{NN} and the stretching vibration frequency $\nu(N_2)$ in these compounds are close to the corresponding values in molecular nitrogen. The C–N_2, O–N_2, and HN–N_2 fragments have a linear configuration‡ (which, as will be shown below, is characteristic of the complexes of nitrogen with metals and their compounds).

The C–N_2, O–N_2, and HN–N_2 bonds are fairly stable: thus in diazomethane $D(H_2C-N_2)$ = 21 kcal mole^{-1} [16] and in nitrous oxide $D(O-N_2)$ = 40 kcal mole^{-1}. The higher energy of the bond of N_2 with carbenes (and the related species O, NH, etc.) and aryl cations, compared with "pure" acceptors such as BF_3, can be accounted for by the additional interaction of the antibonding N_2 orbital and the unshared pairs of p electrons in CH_2, O, or NH. In diazonium salts this role is fulfilled by the π electrons of the aromatic ring, which explains the higher stability of aromatic diazonium salts compared with the aliphatic salts.

It has been shown recently that in many cases the decomposition of diazo-compounds may be reversible. This confirms that it is valid to regard these compounds as "complexes" of molecular nitrogen.

It is now known that certain species are capable of reacting with nitrogen to form diazo-compounds, the process involving a small activation energy. Thus the oxygen atom formed in the singlet state by the photolysis of ozone reacts with N_2 to form N_2O.[17–19] The yield of nitrous oxide varies significantly with reaction conditions: in the gas phase it is only 0.01%,[17] in liquid nitrogen it is 7%,[18] and in solid nitrogen it reaches 35%.[19] This increase in the yield is accounted for by the fact that the energy of the excited N_2O molecule formed in the reaction between N_2 and O is more readily eliminated in the condensed phase.

Moore and Pimentel[20] observed in 1964 the reaction of methylene with N_2 in the solid nitrogen matrix at 20°K. In the photolysis of $CH_2{}^{15}N^{14}N$ in solid molecular nitrogen[14] the infrared spectrum of the products showed, in addition to the absorption bands at 2053 and 2072 cm^{-1}, which are

‡ A cyclic form, as in diazirine $H_2C\langle{}^{N}_{N}\rangle$, is also known. However, linear diazomethane is thermodynamically more stable.

due to the $\nu(N{\equiv}N)$ vibrations in $CH_2{}^{15}N^{14}N$ and $CH_2{}^{14}N^{15}N$ respectively, a band at a frequency of 2096 cm^{-1}, corresponding to the $\nu(N{\equiv}N)$ vibrations in $CH_2{}^{14}N^{14}N$.

The light diazomethane is formed in the reaction

$$CH_2{}^{15}N^{14}N \rightleftarrows CH_2 + {}^{15}N^{14}N \rightleftarrows CH_2{}^{15}N^{14}N$$

$$CH_2 + {}^{14}N^{14}N \rightarrow CH_2{}^{14}N^{14}N$$

It may be supposed that in this case "hot" CH_2 species formed in the photolysis of diazomethane react with nitrogen.

The reaction of methylene with molecular nitrogen in the gas phase was first observed and investigated in detail by Shilov and coworkers [15,21,22]. Both diazomethane and keten, diazirine, and phenylcyclopropane, subjected to photolysis or pyrolysis in an atmosphere of labelled $^{15}N_2$, were employed as sources of methylene in these investigations. In all cases the formation of linear diazomethane ($CH_2{}^{15}N_2$) molecules was observed; the isomeric cyclic diazirine did not form. It was shown that both singlet [$CH_2(s)$] and triplet [$CH_2(t)$] methylene are capable of interacting with nitrogen, the activation energies for the reactions of $CH_2(s)$ and $CH_2(t)$ being respectively about 8 and 16 kcal $mole^{-1}$. Here we may note that, although these quantities are in fact small, they nevertheless exceed the activation energy for the formation of nitrogen complexes with transition metals and their compounds (see p.369). Among the carbenes investigated, methylene proved to be the more active with nitrogen. The rates of the reactions of $(CF_3)CH$ and $(CN)CH$ with N_2 are lower at least by a power of ten than that of CH_2. The remaining carbenes investigated, CH_3CH, C_5H_4, and $CHCOOC_2H_5$, do not react with nitrogen at an appreciable rate.

Recently it was shown that the CH radical [23] and the C atom [24] are also capable of reacting with molecular nitrogen.

An interesting case of the formation of a diazo-compound in the reaction of nitrogen with benzenesulphenium ($C_6H_5S^+$) was recently described [25]. This reaction (if the data are correct) is the first and so far unique example of a reaction of nitrogen with non-metal derivatives in solution at room temperature and at atmospheric pressure of nitrogen. Although the reaction product was not identified, the authors noted that it is capable of entering into the azo-coupling reaction. This suggests that a diazonium salt is formed.

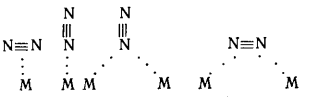
IV. COMPLEXES OF N_2 ON THE SURFACE OF METALS

In the reaction of N_2 with metals there is rapid reversible low-temperature chemisorption and slow high-temperature chemisorption [26]. Surface complexes of molecular nitrogen are then formed together with surface nitrides. Measurements of the heat of chemisorption show that the values of ΔH_{ads} vary in the range between −2 and −20 kcal $mole^{-1}$.

It has been established [27] that several states of chemisorbed nitrogen molecules are realised in the chemisorption of N_2 on the surface of tungsten purified in an ultrahigh vacuum. In one of these states (molecular) nitrogen is completely desorbed at 300°K, while in the other it is desorbed only above 1100°K. If the initial nitrogen is a mixture of $^{14}N_2$ and $^{15}N_2$, the gas desorbed above 1100°K contains $^{14}N^{15}N$. Kinetic studies showed that the desorption of some of the molecules is a second-order process and that of others is a first-order process with respect to the concentration of N_2 on the surface. This finding has been explained [27] by the existence on the surface of both "atomic" (i.e. evidently nitride) nitrogen and its "molecular" form. Possibly isotopic $^{14}N^{15}N$ molecules are formed in the decomposition of the four-membered surface complexes

The possibility of the existence of four-membered nitrogen rings, stabilised by complex formation with transition metals, was demonstrated theoretically in a recent paper [28].

Several structures may be put forward for the surface complexes of molecular nitrogen in low-temperature chemisorption, for example:



So far there has been no direct experimental evidence for the structure of the surface complexes and various authors put forward different considerations in favour of one or other of the structures given above.

By analogy with the bonds of other unsaturated molecules with metals, it may be assumed [29] that the M–N_2 bond forms via the filled π or σ orbitals of N_2 and the free p orbitals of the metal (donor–acceptor interaction) and also the unshared pairs of d electrons of the metal and the antibonding orbitals of N_2 (dative interaction). In this treatment it is of course assumed that the behaviour of the d levels of the surface metal atoms is equivalent to that of free metal atoms.

It may be expected that the polarity of the M–N_2 bond in the surface complex will be different for different metals depending on the relative contributions of the dative and donor–acceptor bonds. In most cases the charge of N_2 should then be negative. It has been shown electrochemically [30,31] that nitrogen undergoes cathodic polarisation on cobalt, copper, silver, and iron. The authors believe that this is associated with the cathodic reduction of the nitrogen molecule: N_2^- ions are formed on the surface of porous metallic films.

Eischens and Jacknow [32], who investigated the chemisorption of N_2 on nickel, observed infrared absorption in the region of 2196 cm^{-1}. With the aid of the $^{14}N_2$ and $^{15}N_2$ isotopes, they showed that this absorption is due to the stretching vibration of the N≡N bond, the frequency of which is greatly reduced compared with that in gaseous nitrogen. The authors believe that the vibration of the N_2 molecule is active in the infrared spectrum because of the formation of the complex Ni–N≡N. Subsequently the infrared spectra of N_2 chemisorbed on different metals (nickel, cobalt, palladium, platinum, iridium) were investigated by other workers [15,33,34,120].

To elucidate the structure of the surface Ni–N_2 complex, molecular nitrogen $^{14}N^{15}N$ was employed [35] (see p. 364). Analysis of the contours of the observed absorption bands of the isotopic molecules $^{14}N^{14}N$, $^{14}N^{15}N$, and $^{15}N^{15}N$ confirmed the linear structure of the complex. In the same study the enthalpy of formation of the complex, Ni + N_2 ⇌ Ni–N_2, was measured and found to be −9.2 kcal $mole^{-1}$ for a surface coverage $\Theta \simeq 0.05$ and −5 kcal $mole^{-1}$ for $\Theta \simeq 0.2$.

According to the data of Eischens and Jacknow [32] and Chernikov and Borod'ko [36], the Ni–N_2 complex is sensitive to molecular hydrogen: when hydrogen is admitted to the system comprising nickel and N_2, the nitrogen absorption band is displaced to higher frequencies, up to 2260 cm^{-1} and then up to 2275 cm^{-1}. Under the action of argon and krypton, the absorption band is displaced towards lower

frequencies[36], to 2170 and 2080 cm^{-1} respectively. It follows from these data that, on being chemisorbed on nickel, hydrogen and the inert gases alter the state of the surface of the metal and the strength of the nickel–nitrogen bond. The direction of the displacement of the vibration frequency of the N≡N bond shows that H_2 behaves as an electron acceptor and argon and krypton behave as electron donors (see p. 365).

The surface complexes of N_2 with palladium and platinum were investigated by van Hardeveld and van Montfoort[34]. Since the extinction coefficients of the bands corresponding to the ν(N≡N) vibration of nitrogen chemisorbed on nickel, palladium, and platinum are similar, one may conclude that the structure of the N_2 complexes with palladium and platinum is also linear.

It is interesting that the complex formation is influenced by the dimensions of the palladium and platinum crystallites: N_2 complexes are formed on particles with effective diameters in the range 15 Å $< d_{eff} <$ 70 Å. Virtually no complexes are formed on metal particles with $d >$ 200 Å and the amount formed on particles with $d <$ 10 Å is very small. These features of the surface nitrogen compounds distinguish them from individual coordination compounds containing a nitrogen molecule as the ligand.

Table 5. Effect of chemisorption on the stretching vibration frequencies of N_2 and CO

Compound	$\nu(N\equiv N)_{ads}$, cm^{-1}	$(\nu_{gas}-\nu_{ads})/\nu_{gas}$	Compound	$\nu(N\equiv N)_{ads}$, cm^{-1}	$(\nu_{gas}-\nu_{ads})/\nu_{gas}$
Ni—N_2	2204	0.055	Ni—CO	2033	0.051
Pd—N_2	2260	0.031	Pd—CO	2085	0.027
Pt—N_2	2230	0.041	Pt—CO	2071	0.034

Carbon monoxide, which is isoelectronic with nitrogen, is also known to form linear complexes on the surface of metals. Comparison of the ν(N≡N) and ν(C≡O) stretching vibration frequencies (Table 5) shows that the reduction of the ν(N≡N) frequency of chemisorbed nitrogen from its frequency in the gas phase is greater than the corresponding shift for carbon monoxide. This is probably associated with the different nature of the upper filled levels of N_2 and carbon monoxide, namely the $3\sigma_g$ orbital of N_2 is bonding and the $3\sigma_g$ orbital of carbon monoxide is non-bonding[4]. While the formation of the π bonds, by which the electron density is displaced to the antibonding orbitals of N_2 and carbon monoxide, lowers the stretching vibration frequencies, the formation of σ bonds has different effects[37] on the N≡N and C≡O bond strengths and hence the ν(N≡N) and ν(C≡O) frequencies. In the coordination of N_2 the formation of a σ bond leads to an electron shift from the bonding $3\sigma_g$ orbital and an additional lowering of the ν(N≡N) frequency, while in the case of carbon monoxide the formation of a σ bond is associated with a decrease of electron density in the non-bonding 3σ orbital§.

§ Carbon monoxide in the gas phase is characterised by absorption at 2146 cm^{-1} in the infrared spectrum, while in the complex BH_3...CO (formed via a σ bond) the ν(C≡O) vibration frequency is 2164 cm^{1}. Possibly this is due to the fact that the 3σ(CO) level is weakly antibonding.

In the interaction of carbon monoxide with transition metals the displacement of the ν(C≡O) frequency is a result of the superposition of two opposed effects, and the fact that ν(C≡O) is reduced on complex formation is evidence that the π dative component makes a greater contribution to the bond with the transition metal than the σ donor component. For the nitrogen molecule, both types of interaction lead to a decrease of frequency. Therefore, in contrast to carbon monoxide, in the case of N_2 one should always expect a bathochromic shift of the ν(N≡N) frequency on complex formation[37].

V. COMPLEXES OF NITROGEN WITH TRANSITION METAL COMPOUNDS (NITROGENYLS)

1. SYNTHESIS AND CHEMICAL PROPERTIES OF NITROGENYLS

Nitrogenyl Complexes of Ruthenium

$[RuN_2(NH_3)_5]X_2$. This, the first of the known complexes of molecular nitrogen with transition metal compounds, was obtained by Allen and Senoff[38] in 1965 by the reaction of $RuCl_3$ with hydrazine hydrate in aqueous solution; it is then possible to isolate from the solution the saltlike compounds $[RuN_2(NH_3)_5]X_2$ (X = Cl^-, Br^-, I^-, or BF_4^-). Subsequently the same complexes were obtained by the action of hydrazine hydrate on other ruthenium(III) and ruthenium(IV) salts and in the reaction of sodium azide with aquopentammineruthenium(III) methanesulphonate[39].

The complexes $[RuN_2(NH_3)_5]X_2$ were also obtained when all the ligands, except nitrogen, were substituted by ammonia[40] in the non-saltlike complexes $RuN_2Cl_2(H_2O)THF$ (see p. 361)[THF = tetrahydrofuran (Ed. of Translation)], by passing nitrogen[41] into an aqueous solution of $[Ru(NH_3)_5H_2O]Cl_2$, and by the action of ammonia[42] and zinc dust on $RuCl_3.3H_2O$.

The salts of pentammineruthenium nitrogenyls have been isolated in a crystalline state. They are thermally stable and relatively stable in aqueous solutions, but, under the action of a number of compounds, molecular nitrogen may be displaced by other ligands[39].

The infrared spectra of the complexes show an absorption band in the region 2105–2167 cm^{-1} (Table 6), which corresponds to the N≡N stretching vibration, and in the electronic spectra there are absorption bands with maxima at 221 and 463 nm.

According to the data of Allen and Senoff[38], under the action of $NaBH_4$ nitrogen in the complex may be reduced to ammonia either completely or, as stated subsequently[39], partially. However, these results were not confirmed[40]. It has been established by mass-spectrometric analysis that ammonia in the product of the reaction of $[Ru^{15}N_2(NH_3)_5]X_2$ with $NaBH_4$ is not enriched in labelled $^{15}NH_3$ in excess of the natural content, i.e. N_2 in the complex is not reduced.

It also proved impossible to reduce the nitrogen in the complex by reducing agents such as $CrCl_2$, EtMgBr, $Na_2S_2O_4$, and zinc and hydrochloric acid[40]. Allen and coworkers[38,39] and subsequently Chatt and coworkers[45] stated that, under the action of sulphuric and hydrochloric acids, only part of the coordinated nitrogen in the nitrogenyl complex is evolved in the form of N_2 (i.e. the coordinated nitrogen reacts at least partially with the acid), but these results appear very doubtful, particularly in view of

the negative findings of Borod'ko et al.[40] in the study of the reduction of a nitrogenyl complex¶.

$RuN_2Cl_2L_3$ (L = H_2O, NH_3, Py, THF, etc.). These complexes were the first to be obtained directly from molecular nitrogen. They are formed[40,43,44] by the reduction of $RuCl_3$ and $RuCl_3OH$ with amalgamated zinc in the presence of nitrogen in tetrahydrofuran (THF). The yield of the nitrogen complex increases with the N_2 pressure and becomes almost quantitative at pressures in excess of 40–60 atm.

Table 6. Stretching vibration frequencies of the N≡N bond in nitrogenyl complexes

Compound	ν (N≡N), cm^{-1}	References
$FeN_2(PPh_2Et)_3H_2$	2055	59
$FeN_2(PPh_2Et)_2H_2$	1939	59
$FeN_2(PPh_3)_3H_2$	2074, 2053, 2039 *	85
$FeN_2(PPh_3)_3H_2$ (in toluene)	2068	
$[RuN_2(NH_3)_5]Cl_2$	2105	38, 39
$[RuN_2(NH_3)_5]Br_2$	2114	38, 39
$[RuN_2(NH_3)_5]I_2$	2129	38, 39
$[RuN_2(NH_3)_5](BF_4)_2$	2144	38, 39
$[RuN_2(NH_3)_5](BF_6)_2$	2167	38, 39
$[RuN_2(NH_3)_5]^{2+}$ (в H_2O)	2130	38, 39
$RuN_2(NH_3)_3Cl_2$	2080	40, 44
$RuN_2(NH_3)_2H_2OCl_2$	2090	40, 44
$RuN_2(H_2O)Cl_2 \cdot THF$	2153	40, 44
$RuN_2(PPh_3)_3H_2$	2147	49, 50
cis-$[RuN_2(en)_2H_2O][B(C_6H_5)_4]_2$	2130	51
cis-$[Ru(N_2)_2(en)_2][B(C_6H_5)_4]_2$	2220, 2190	51
$[OsN_2(NH_3)_5]Cl_2$	2012**	52, 53, 54
$[OsN_2(NH_3)_5]Br_2$	2028**	52, 53, 54
$[OsN_2(NH_3)_5]I_2$	2033**	52, 53, 54
$[OsN_2(NH_3)_5](ClO_4)_2$	2051**	53
$[OsN_2(NH_3)_5](BF_4)_2$	2055	53
$[OsN_2(NH_3)_5](BPh_4)_2$	2061	53
$[OsN_2(NH_3)_5]^{2+}$ (в H_2O)	2032	54
$[Os(N_2)_2(NH_3)_4]Cl_2$	2120, 2175	54, 55
$CoHN_2(PPh_3)_3$	2088	61,62,63,64
$CoHN_2(PPh_3)_2(PBu_3)$	2075	84
$CoHN_2(PPh_3)(PBu_3)_2$	2061	84
$CoHN_2(PBu_3)_3$	2048	84
$CoHN_2[P(p\text{-}CH_3C_6H_4)_3]_3$	2073	68
$CoHN_2[P(Ph_2C_6H_5)]_3$	2060	68
$CoHN_2[P(p\text{-}C_6H_5)_3]_3$	2032	68
$CoHN_2[P(C_2H_5)_3]_3$	2032	68
$RhN_2Cl(PPh_3)_2$	2152	37, 76
$IrN_2Cl(PPh_3)_2$	2185	37, 74, 75
$NiN_2[P(C_6H_{11})_3]_2$	2028	77

* The vibration frequencies ν(N≡N) of the crystalline complex due to Davydov splitting.
** The vibration frequency of the Davydov component with maximum intensity.

The composition of the complex obtained in tetrahydrofuran solution corresponds to the formula $RuN_2Cl_2(H_2O)_2THF$. This complex is thermally much less stable than the pentammine and decomposes slowly with evolution of hydrogen even at room temperature. It has been established[40,44] that, when the complex is acted upon by bases (ammonia, pyridine, ethylenediamine, etc.), the ligands at the ruthenium atom are substituted with retention of part of the nitrogen in the coordination sphere. A whole series of $RuN_2Cl_2L_3$ with different ligands L were obtained in this way, which permitted certain conclusions about the nature of the ruthenium–nitrogen bond. It again proved impossible to reduce the nitrogen in the complex by various reducing agents.

¶ In fact, recently Chatt and coworkers[46,47] found that the results of earlier studies[38,39,45] showing the reduction of N_2 in the complex and also the interaction of nitrogenyl complexes with acids are erroneous, due to the presence of large amounts of hydrazine as an impurity in the complex obtained by Allen's method.

Other Complexes of Nitrogen with Ruthenium Compounds

It has been established[44,48] that nitrogen is coordinated to ruthenium when $RuCl_3$ is reduced by reducing agents such as C_2H_5MgBr, C_6H_5MgBr, $TiCl_3$, Na_2S_2, and Na_2S. The complexes formed under these conditions were not isolated but there are indications that in some cases they contain ligands other than those discussed above. Thus, when sulphides are used, the complexes probably contain sulphur together with nitrogen.

$RuN_2(PPh_3)_3H_2$. It has been found[49] that nitrogen forms a complex on interaction with the ruthenium compound having the hypothetical formula $Ru(PPh_3)_4H_2$. This complex was isolated[50] after the reaction of $(PPh_3)RuHCl$ with $AlEt_3$ in the presence of nitrogen in ether. The complex corresponds to the formula $RuN_2(PPh_3)_3H_2$. It is sensitive to air and is stable in an atmosphere of nitrogen at room temperature.

Dinitrogenyl complex of ruthenium(II). The interaction of *cis*-$[Ru(en)_2N_3N_2]^+$ with HNO_2 yielded a complex containing two nitrogen molecules in the coordination sphere of ruthenium in the *cis*-position[51]. The reaction takes place according to the equation
cis-$[Ru(en)_2N_3N_2]^+ + HNO_2 \rightarrow$ *cis*-$[Ru(en)_2(N_2)_2]^{2+} + N_2O$.
The infrared spectrum of the complex shows two absorption bands at 2220 and 2190 cm^{-1}. In aqueous solution the dinitrogenyl complex decomposes irreversibly with formation of *cis*-$[Ru(en)_2H_2ON_2]^{2+}$; the product of this reaction was isolated as the tetraborate [ν(N≡N) = 2130 cm^{-1}].

Osmium Complexes

Ammine nitrogenyls. The first complexes of nitrogen with osmium compounds were obtained[52] by the reaction of hydrazine with osmium compounds such as K_2OsCl_6, $OsCl_4$, $OsCl_3OH$, i.e. a reaction analogous to that whereby ruthenium nitrogenyls are synthesised by the method of Allen and Senoff. If is interesting that, in contrast to ruthenium compounds, the formation of several complexes of molecular nitrogen with osmium was observed in this case. Subsequently it was established[53,54] that the main product is the analogue of pentammineruthenium nitrogenyl $[OsN_2(NH_3)_5]X_2$ with ν(N≡N) at 2012 cm^{-1} in the infrared spectrum. The less stable dinitrogenyl complex $[Os(N_2)_2(NH_3)_4]X_2$ probably forms at the same time.

In a recent communication[55] the synthesis of the dinitrogenyl complex of osmium by another method was described. When nitrous acid acts on an aqueous solution of $[OsN_2(NH_3)_5]X_2$, a crystalline product is formed, whose composition corresponds to the formula $[Os(N_2)_2(NH_3)_4]X_2$ (X = Cl^-, Br^-, or I^-) according to elemental analysis. The infrared spectrum of this compound shows absorption bands at 2120 and 2175 cm^{-1}, which is evidence of the *cis*-configuration of this dinitrogenyl complex.

In the crystalline state the complex $[OsN_2(NH_3)_5]X_2$ is exceptionally stable: it decomposes above 200°C. In aqueous solution the evolution of nitrogen is catalysed by various metal ions (Ag^+, Cu^{2+}).[56] The thermal decomposition of the complex in aqueous solution is inhibited by carbon monoxide[57]. This is probably due to the binding of catalytically active species into inactive carbonyls.

Other Complexes of Osmium with Molecular Nitrogen

Nitrogenyl complexes of osmium have been obtained[44] directly from molecular nitrogen in the reduction of $OsCl_3OH$ by amalgamated zinc in tetrahydrofuran solution. Examination of the vibration spectra of the reduction products led to the conclusion that several nitrogen-containing complexes are formed. The complexes were not identified but it may be supposed that they are similar in composition to the ruthenium complexes formed under analogous conditions†.

Dinuclear Complexes of Ruthenium and Osmium

It has been stated[58] that the formation of a complex in which two metal atoms are linked to nitrogen is possible. The dinuclear ruthenium complexes are formed when the pentammineruthenium nitrogenyl $[RuN_2(NH_3)_5]X_2$ reacts with the aquopentammine complex $[Ru(NH_3)_5H_2O]X_2$. In aqueous solution the complex $[(NH_3)_5RuN_2Ru(NH_3)_5](BF_4)_4$ has an intense absorption band at 262 nm.

The formation of dinuclear complexes in aqueous solutions is an equilibrium process: when the concentration of $\{[Ru(NH_3)_5]_2N_2\}^{4+}$ is reduced, the complex dissociates into the mononuclear nitrogenyl and $[Ru(NH_3)_5H_2O]^{2+}$.

It has been suggested[56] that the decomposition of $[OsN_2(NH_3)_5]^{2+}$ in the presence of silver(I) and copper(II) salts takes place via the intermediate formation of the complexes $[(NH_3)_5OsN_2Cu]$ and $[(NH_3)_5OsN_2Ag]$.

Nitrogenyl Complexes of Iron

The complexes of nitrogen with iron compounds are of interest, since their formation in the enzyme systems of nitrogen-fixing bacteria probably constitutes the first stage in the biological fixation of nitrogen.

A complex of a dihydride derivative of iron(II) with nitrogen was synthesised by Sacco and Aresta[59] by the reaction of N_2 with $FeH_2[P(C_6H_5)_2R]_3$ (R = ethyl or butyl). A yellow crystalline complex, decomposing at 80°C with evolution of nitrogen and hydrogen, was then isolated. The complex is diamagnetic and is characterised by an intense absorption band in the infrared at 2055–2060 cm^{-1}. The interaction of this complex with triethylaluminium gave the compound $FeH_2N_2[P(C_6H_5)_2R]_2$, whose infrared spectrum shows a band at a frequency of 1989 cm^{-1}, which has been assigned[59] to the stretching vibrations of the nitrogen–nitrogen bond.

The formation of nitrogen complexes with iron compounds, produced by the action of N_2 on low-valence derivatives of iron, has also been described[60]. Thus the reaction of nitrogen with the iron(0) complex of cyclooctadiene or with tris-π-allyliron in the presence of phosphines yields nitrogen-containing complexes (a band at 2038 cm^{-1} is observed in the infrared spectrum), which, however, could not be isolated in a pure state.

Complexes of Nitrogen with Cobalt Compounds

The formation of complexes of molecular nitrogen with cobalt compounds has been described[61–65]. Yamamoto et al.[61] obtained the cobalt complex at atmospheric nitrogen pressure by the reaction of cobalt(III) acetylacetonate with ethoxydiethylaluminium in the presence of triphenylphosphine in ether or toluene. In accordance with the results of elemental analysis, the formula $CoN_2(PPh_3)_3$ was ascribed to the yellow crystals isolated from the solution. In the absence of air the complex is comparatively stable, but decomposes with evolution of nitrogen at 80°C.

A nitrogenyl complex of cobalt was also obtained by Misono and coworkers[63,64] by the action of nitrogen on a hydride derivative of cobalt. The hydride was synthesised by passing H_2 into a mixture of cobalt(III) acetylacetonate, triphenylphosphine, and tri-isobutylaluminium in ether at 10°C. In the interaction of this hydride solution with nitrogen the colour of the former changes from yellow to red and orange crystals can be isolated from the reaction mixture; their infrared spectrum shows absorption at 2088 cm^{-1}. Evidently this complex is identical with that obtained by Yamamoto and the reaction involves the displacement of hydrogen by nitrogen from cobalt hydride. It was concluded[63,64] that the product of the reaction with nitrogen is a mixture of $CoN_2(PPh_3)_3$ and $CoHN_2(PPh_3)_3$.

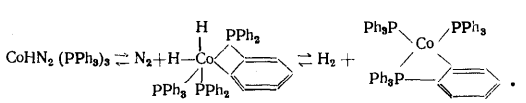
The Italian workers Sacco and Rossi[65,66] stated that nitrogen reacts reversibly with the trihydride complex of cobalt to form a cobalt(I) nitrogenyl complex:

$$CoL_3H_3 + N_2 \rightleftarrows CoHN_2L_3 + H_2.$$

where L = PPh_3 or PPh_2Et. This complex consists of orange crystals, which are fairly stable in air and soluble in non-polar solvents. An intense absorption band at 2080–2084 cm^{-1} in the infrared spectrum of the complex corresponds to the stretching vibrations of the nitrogen. The complex is diamagnetic; in accordance with the formula quoted, 1.5 moles of gas consisting of nitrogen and hydrogen in the proportions $N_2 : H_2 = 2 : 1$ are evolved per mole of the complex in its decomposition at 100–150°C.

Since the complex of Sacco and Rossi is very similar in its properties to the complex obtained by the Japanese workers[61–64], it may be supposed that the two are identical. Indeed X-ray diffraction analysis showed[67] that the complex obtained by a similar procedure[61] has the formula $CoHN_2(PPh_3)_3$. In a recent study by NMR Misono and coworkers[68] obtained further confirmation that this complex contains a hydride hydrogen atom and therefore the previously proposed formula[61] $CoN_2(PPh_3)_3$ may be regarded as erroneous.

The study of the isotope exchange of deuterium with the complex showed[69] that not only the hydride hydrogen atom but also the hydrogen atoms in the *ortho*-positions of the phenyl ring of triphenylphosphine participate in the reaction, possibly according to the mechanism



The complex $CoHN_2(PPh_3)_3$ reacts reversibly with H_2, ethylene, and ammonia with displacement of nitrogen[62]; it reacts irreversibly with carbon monoxide to form a carbonyl[70], and also with carbon dioxide to form the formate complex[71] $CoHCO_2(PPh_3)_3$.

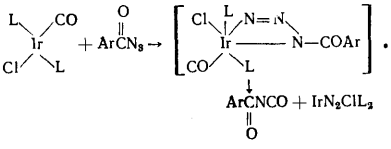
The cobalt nitrogenyl complex catalyses the hydrogenation of ethylene[72], the oxidation of triphenylphosphine to triphenylphosphine oxide, and the dimerisation of ethylene and propene[73].

† Recently a number of nitrogenyl complexes of osmium(II) of the type $OsN_2X_2(PR_3)_3$, where X = Cl or Br, were obtained[121] by the method of Borod'ko et al.[44]

The Nitrogenyl Complexes of Indium(I)

Collman and Kang[75] synthesised the complex $IrN_2Cl(PPh_3)_2$ by the reaction of azides with the carbonyl complex of iridium. The band at 2105 cm^{-1} in the infrared spectrum of this complex corresponds to the N≡N stretching vibrations. The complex is stable in the crystalline state at room temperature, but its solutions in chloroform and toluene decompose slowly with evolution of nitrogen.

A study of the mechanism of the formation of the complex IrN_2L_3 showed[75] that the reaction takes place in the coordination sphere of iridium without liberation of N_2 and CO molecules into the solution. The reaction also yields the isocyanate:



The Nitrogenyl Complex of Rhodium(I)

Using a procedure similar to that employed in the synthesis of the iridium complex of N_2, the analogous N_2 complex of rhodium(I) $RhN_2Cl(PPh_3)_2$ was synthesised[76]. A band at 2152 cm^{-1} in the infrared spectrum of the complex corresponds to the N_2 vibrations. The complex is less stable than its iridium analogue. Although in the solid state (yellow crystals) the complex remains unchanged at room temperature in the absence of air, its solutions in chloroform, benzene, or toluene decompose rapidly with evolution of nitrogen

Complexes of Nickel(0)

The first nitrogen complex of zerovalent nickel was synthesised in 1968[77]. This is a dinuclear complex which is formed on mixing nickel acetylacetonate with trimethylaluminium in the presence of nitrogen and tricyclohexylphosphine. The reaction proceeds according to the equation

$$2Ni(acac)_2+4(C_6H_{11})_3P+4Al(CH_3)_3+N_2\longrightarrow N_2[Ni(P(C_6H_{11})_3)_2]_2+ +4(CH_3)_2Al(acac)+4CH_3.$$

The yield of the complex, which consists of dark red crystals, reaches 40%.

In benzene solution the dinuclear complex dissociates reversibly to the mononuclear complex $NiN_2[P(C_6H_{11})_3]_2$ and $Ni[P(C_6H_{11})_3]_2$. The infrared spectrum of the mononuclear nitrogenyl shows absorption at 2028 cm^{-1}, which has been assigned to the vibration of the N≡N bond.

Nitrogen Complexes of Manganese(II)

It has been stated[78] that oxygen, carbon monoxide, and nitrogen combine reversibly with manganese(II) compounds forming 1 : 1 adducts. In contrast to all the mononuclear nitrogenyl complexes known hitherto, the infrared spectrum of the adduct with nitrogen does not contain a band in the region 2000–2200 cm^{-1}. It is surprising that the infrared spectrum of the carbon monoxide complex also lacks a band corresponding to the CO vibration. This finding is so unusual, that its validity appears questionable.

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Thus several methods are known at present for the synthesis of complexes containing molecular nitrogen in the coordination sphere of the metal and the complexes can be obtained both by the addition of molecular nitrogen and by indirect methods, in which nitrogen is formed directly in the coordination sphere of the metal.

The coordination of molecular nitrogen can occur at the instant of the reduction of transition metal salts (as in the synthesis of carbonyls) by the substitution of ligands in certain low-valence metal derivatives, and by direct interaction with coordination-unsaturated systems.

Although considerable advances have in fact been achieved in the synthesis of nitrogenyl complexes, many features of these compounds still remain obscure. For example, the failure to synthesise the complex by one of the standard methods may imply either that the complex is unstable or that the method is unsuitable for the given compound.

2, THE STRUCTURE OF THE COMPLEXES AND THE NATURE OF THE M–N_2 CHEMICAL BOND

X-Ray Diffraction Analysis of Nitrogenyls

At present only two compounds have been analysed by X-ray diffraction: $[RuN_2(NH_3)_5]X_2$,[79,80] and $CoHN_2(PPh_3)_3$.[67] The ruthenium complexes crystallise with a cubic lattice containing four molecules per unit cell. Bottomley and Nyburg[79,80] showed that the ruthenium ion is surrounded octahedrally by nitrogen atoms [r(Ru–N) = 2.10 Å], molecular nitrogen is coordinated to the two metals almost linearly, and the distance between two adjacent nitrogen atoms in the RuNN fragment is 1.12 Å. While the linear coordination of the N_2 molecule has been established unambiguously, the interatomic r(Ru–N) and r(N–N) distances have been determined only approximately due to the statistically disordered arrangement of the molecules in the lattice.

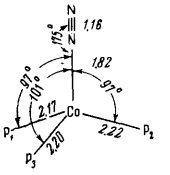


Figure 4. The structure of $CoHN_2(PPh_3)_3$.

The $CoHN_2(PPh_3)_3$ crystals were obtained[67] in two modifications, one of which is not susceptible to accurate analysis, while the other (it is noteworthy that subsequently it could not be synthesised again) has the structure of a distorted trigonal bipyramid (Fig. 4).

It should be noted that both in the cobalt complex and probably in the ruthenium nitrogenyl the M–N–N fragment is not rigorously linear. The Co–N–N angle is[67] 175° ± 4°.

In the nitrogenyl complexes of ruthenium and cobalt the r(N–N) bond length is greater than in the nitrogen molecule in the gas phase [r(N≡N) = 1.097 Å]. However, it is

significantly smaller than the nitrogen–nitrogen interatomic distance in azo-compounds; therefore it can be assumed that the multiplicity of the nitrogen–nitrogen bond in $[RuN_2(NH_3)_5]X_2$ and $CoHN_2(PPh_3)_3$ is close to three.

Infrared Absorption Spectra of Nitrogenyl Complexes

Infrared spectroscopy has found wide application in the identification and study of nitrogenyl complexes. As a result of the coordination of the N_2 molecule, an intense absorption band due to the stretching vibrations of the NN bond appears in the spectrum (2000–2200 cm^{-1}).

The vibration frequency of the N≡N bond in the nitrogen molecule is known to be 2331 cm^{-1}, while those of the N=N bonds in azo-compounds are in the range 1400–1600 cm^{-1}.[81,82] Thus the frequency range of the NN bond vibrations in nitrogenyl complexes (Table 6) corresponds to a bond order close to 3, in agreement with the X-ray diffraction studies.

Group-theoretical Analysis of the NN Bond Vibrations in Nitrogenyl Complexes

In principle molecular nitrogen can form with transition metals complexes having different structures (I)–(X) (Fig. 5). [So far compounds of types (I), (III), and (IX) have been synthesised.] On the basis of the local symmetry of these models, it is possible to determine under what conditions the nitrogen–nitrogen bond stretching vibrations will be active in the infrared absorption spectrum.

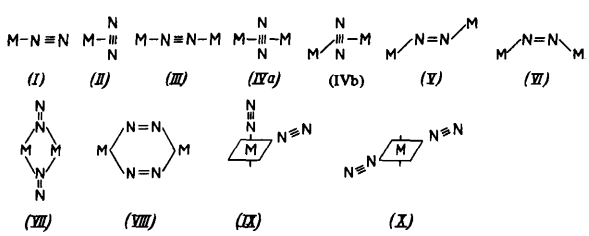


Figure 5. Possible structures of the nitrogen complexes.

The results of such analysis are presented in Table 7, which shows (fifth and sixth columns) that nitrogen–nitrogen bond vibrations in complexes of the type (I), (II), (IVb), (VI), and (VII)–(X) are active in the infrared spectrum, while the vibrations of complexes of the type (III), (IVa), and (V) are inactive. It should be noted that this conclusion was obtained on the assumption that in dinuclear complexes the ligands of both metal atoms and the metal atoms themselves are the same. On the other hand, when the ligands or the metal atoms are different, the symmetry is decreased and the stretching vibrations of the NN bond may be active in the infrared spectrum.

Spectra of Nitrogenyl Complexes Containing Nitrogen Isotopes

The validity of the assignment of the absorption bands in the range 2000–2200 cm^{-1} (Table 6) to the stretching vibrations of the N≡N bond is unambiguous, particularly since the replacement of $^{14}N{\equiv}^{14}N$ by $^{15}N{\equiv}^{15}N$ or $^{14}N{\equiv}^{15}N$ results in a decrease of the vibration frequency by 60–70 cm^{-1} or 30–35 cm^{-1} respectively, which agrees well with the calculated isotopic shift[40,43,44,49,52,54]. The ability to synthesise nitrogenyl complexes containing nitrogen-29 only, made it possible in some cases to establish the structure of the $M-N_2$ fragment.

Table 7. Types of stretching vibrations of the nitrogen–nitrogen bonds active in the infrared spectrum

Structure	Symmetry point group	Complete representation	Types of vibrations active in infrared spectrum	ν_s (NN)	ν_{as} (NN)
I	$C_{\infty v}$	$2A+E$	$2A+E$	A	—
II	C_{2v}	$2A_1+B_2$	$2A_1+B_2$	A_1	—
III	$D_{\infty h}$	$2A_{1g}+A_{1u}+E_{1g}+E_{1u}$	$A_{1u}+E_{1u}$	—	—
IVa	D_{2h}	$2A_g+B_{3g}+B_{1u}+B_{2u}+B_{3u}$	$B_{1u}+B_{2u}+B_{3u}$	—	—
IVb	C_{2v}	$3A_1+A_2+B_1+B_2$	$3A_1+B_1+B_2$	A_1	—
V	C_{2h}	$3A_g+A_u+2B_u$	A_u+2B_u	—	—
VI	C_{2v}	$3A_1+A_2+2B_2$	$3A_1+2B_2$	A_1	—
VII	D_{2h}	$3A_g+2B_{1u}+B_{2g}+2B_{2u}+2B_{3g}+2B_{3u}$	$2B_{1u}+2B_{2u}+2B_{3u}$	—	B_{3u}
VIII	D_{2h}	$3A_g+A_u+B_{1g}+2B_{1u}+2B_{2u}+2B_{3g}+B_{3u}$	$A_u+2B_{1u}+2B_{2u}+B_{3u}$	—	B_{3u}
IX	C_{2v}	$4A_1+A_2+3B_1+B_2$	$4A_1+3B_1+B_2$	A_1	B_1
X	D_{2h}	$2A_g+B_{2g}+B_{3g}+2B_{1u}+2B_{2u}+2B_{3u}$	$2B_{1u}+2B_{2u}+2B_{3u}$	—	B_{1u}

The spectra of ruthenium complexes containing $^{14}N^{14}N$ and $^{14}N^{15}N$ have been investigated[40,44]. The activity of the NN bond vibrations in the infrared spectrum may be evidence of the formation of complexes of type (I) or (II) (Fig. 5). If the complexes have the linear structure (I), then there are two equally probable possibilities of the coordination of nitrogen-29: either $Ru-{}^{14}N{\equiv}{}^{15}N$ or $Ru-{}^{15}N{\equiv}{}^{14}N$, and the $\nu(N{\equiv}N)$ vibration frequencies may differ by 3–10 cm^{-1}. For the structure of type (II), the band in the RuN_2 spectrum should of course not be split. Analysis[44] of the observed spectrum of the complex $RuN_2Cl_2(NH_3)_3$ showed that the absorption band corresponding to $\nu(^{14}N{\equiv}^{15}N)$ results from superposition of two bands with a splitting of 4–6 cm^{-1}. Hence it was concluded that the Ru–N≡N fragment is linear. Similar results were obtained[40] also for pentamminenitrogenylruthenium, in agreement with X-ray diffraction data[79,80]. The N≡N stretching vibration frequencies of the complexes $[RuN_2(NH_3)_5]I_2$ containing nitrogen isotopes proved to be as follows:

$$\left.\begin{array}{ll}[Ru(NH_3)_5N^{14}{\equiv}N^{14}]I_2 & 2132\\ [Ru(NH_3)_5N^{14}{\equiv}N^{15}]I_2 & 2098\end{array}\right\}\Delta\nu{=}4\ cm^{-1}$$

$$\left.\begin{array}{ll}[Ru(NH_3)_5N^{15}{\equiv}N^{14}]I_2 & 2094\\ [Ru(NH_3)_5N^{15}{\equiv}N^{15}]I_2 & 2060\ cm^{-1}\end{array}\right\}$$

The force constants (10^6k, cm^{-2}) of the bonds in the Ru–N≡N fragment were calculated from these experimental values[40]: $k_{NN} = 29.3$, $k_{RuN} = 5.5$, and $k_{NN,RuN} = 1.2$.

It is interesting that these force constants of the bonds in the Ru–N≡N fragment of the nitrogenyl complex proved to be close to the corresponding force constants for the diazo-group C–N≡N in diazomethane[83]: $k_{NN} = 27.7$, $k_{CN} = 7.97$, and $k_{CN,NN} = 1.5$.

In the infrared spectra of the crystalline complexes $CoHN_2(PPh_3)_3$ [84] and $FeH_2N_2(PPh_3)_3$ [85] the half-widths of the bands due to the vibrations of the $^{14}N{\equiv}^{14}N$, $^{14}N{\equiv}^{15}N$, and $^{15}N{\equiv}^{15}N$ bonds are the same, the half-width amounting to

5–6 cm^{-1}. Thus one may conclude that the band corresponding to the $^{14}N\equiv{}^{15}N$ vibration in the complexes is not split. When the iron compounds are dissolved in toluene, the absorption bands corresponding to the N≡N vibration become appreciably broader (up to 16 cm^{-1}) (Fig. 6).

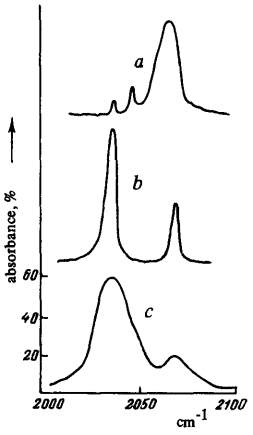


Figure 6. Absorption bands associated with the stretching vibrations of the N≡N bond in $FeH_2N_2(PPh_3)_3$: *a*) crystalline $FeH_2N_2(PPh_3)_3$; *b*) crystalline product containing $FeH_2(^{14}N^{15}N)(PPh_3)_3$ and $FeH_2(^{14}N^{14}N)(PPh_3)_3$; *c*) spectrum of a mixture of $FeH_2(^{14}N^{15}N)(PPh_3)_3$ and $FeH_2(^{14}N^{14}N)(PPh_3)_3$ in toluene solution at 10°C.

To account for the results obtained[85], it has been suggested that association complexes are formed in the crystals.

Borod'ko et al.[54] have quoted the vibration frequencies of a series of pentammineosmium nitrogenyls with different nitrogen isotopes in the range 60–3700 cm^{-1} and have given the assignments of these bands. The Os–N≡N fragment is characterised by three absorption bands corresponding to $\nu(NN) = 2010–2034$ cm^{-1}, $\nu(Os–N_2) = 500–518$ cm^{-1}, and $\delta(OsNN) = 245$ cm^{-1}.

Absorption Band Intensities $\mathcal{J}(N\equiv N)$

The integral intensity of the absorption band corresponding to the stretching vibration of the N≡N bond can be used to assess the structure of the $M–N_2$ fragment. In the case of linear coordination of the type M–N≡N the nitrogen–nitrogen bond is appreciably polarised and probably in all nitrogen complexes with a linear structure the intensity $\mathcal{J}(N\equiv N)$ will be high. By analogy with the π-complexes of symmetrical olefins and acetylenes, one may expect that the intensity $\mathcal{J}(N\equiv N)$ in the spectra of π-complexes of the type $M-\overset{N}{\underset{N}{\|}}$ will be very low.

Table 8, where the intensities for a number of nitrogenyls are listed, shows that $\mathcal{J}(N\equiv N)$ varies in the range $2.7 \times 10^4–8.5 \times 10^4$ litre $mole^{-1}$ cm^{-2}, which is characteristic of the intensities of the stretching vibrations of nitrogenyls known to have a linear structure and also of carbonyls. Hence one may conclude that the linear structure M–N≡N obtains in the complexes $[OsN_2(NH_3)_5]X_2$, $RhN_2Cl(PPh_3)_2$, $IrN_2Cl(PPh_3)_2$, and $Fe_2H_2N_2(PPh_3)_3$.

It is interesting that the surface complexes of nitrogen on metallic nickel, palladium, and platinum appear to have $\mathcal{J}(N\equiv N)$ intensities similar to those quoted above.

Table 8. Integral intensities of the bands due to the stretching vibrations of the N≡N bond

Compound	$\nu_{(N\equiv N)}$, cm^{-1}	$\mathcal{J}_{(N\equiv N)}$, 10^4 litre $mole^{-1}$ cm^{-2}	Refs
$FeN_2H_2(PPh_3)_3$	2066	4.9	85
$[RuN_2(NH_3)_5]Br_2$	2106	2.9	54
$[OsN_2(NH_3)_5]Cl_2$	2012	6.1	54
$[OsN_2(NH_3)_5]^{2+}$	2030	8.5	54
$RhN_2(PPh_3)_2Cl$	2152	3.4	37
$IrN_2(PPh_3)_2Cl$	2095	2.7	37

Dependence of the $\nu(N\equiv N)$ Frequency on the Radii of the Anions and the Nature of the Ligands

The N≡N bond stretching vibration frequency in the salts $[RuN_2(NH_3)_5]X_2$ and $[OsN_2(NH_3)_5]X_2$ depends on the anion X^-: the greater the ionic radius of the anion the higher is the vibration frequency[87] (Fig. 7). This relation may be due to the fact that, as the radius of the X^- anion decreases, the effective electrostatic field strength increases. Accordingly there is an increase in the contribution of the more polar structure (b) which is characterised by a lower $\nu(N\equiv N)$ vibration frequency:

$$\underset{(a)}{L_5M–N\equiv N} \longleftrightarrow \underset{(b)}{L_5M=\overset{+}{N}=\overline{N}}$$

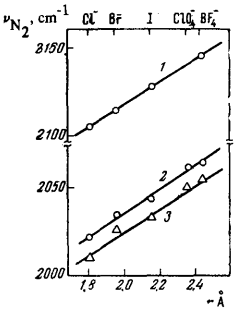


Figure 7. Dependence of the stretching vibration frequency $\nu(N\equiv N)$ on the radius of the anion: 1) $[RuN_2(NH_3)_5]X_2$; 2) and 3) $[OsN_2(NH_3)_5]X_2$. The variation of the frequencies of the two components of $\nu(N\equiv N)$, due to Davydov splitting, is shown for the osmium complex.

In the series of non-saltlike compounds of the type $RuN_2Cl_2L_3$ the N≡N stretching vibration frequency depends on the nature of the ligand L: the frequency falls with increasing basicity of the ligand[40] (Table 9). Misono et al.[87] who investigated the compounds $CoHN_2L_3$ in which L = $P(p\text{-}CH_3C_6H_4)_3$, $P[(C_6H_5)_2C_2H_5]_3$, $P(n\text{-}C_4H_9)_3$, or $P(C_2H_5)_3$ arrived at a similar conclusion; this dependence is evidence

of a significant contribution of the d_π–p_π interaction in the formation of the M–N_2 bond. Under the influence of donor ligands, the contribution of structure (b) falls.

It also follows from the work of Misono et al.[87] that the steric factor plays a major role in the formation of nitrogen complexes. Thus nitrogen complexes are not formed with $P(C_6H_5)_2H$ and $P(C_6H_5)_2CH_3$ and only the compound $CoHL_4$ (L = phosphine) is produced. Thus in the more bulky phosphines (PPh_3, $PPh_2C_2H_5$, etc.) one coordination site is occupied by molecular nitrogen because it is inaccessible to the phosphine molecule, although the metal–phosphine bond is probably stronger than the metal–nitrogen bond.

Table 9. Variation of the stretching vibration frequency ν(N≡N) of ruthenium nitrogenyls $RuN_2Cl_2L_3$ with the basicity of the ligand (L)

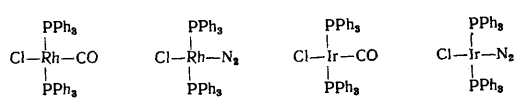
$RuN_2Cl_2L_3$	
ligand (L),	ν (N≡N), cm^{-1}
$3H_2O$	2163
$2H_2O \cdot THF$	2153
$(CH_3)_2NCHO$*	2123
C_5H_5N *	2115
$2NH_3 \cdot H_2O$	2090
$3NH_3$	2080
$C_2H_4(NH_2)_2$	2085

* The number of ligands was not determined.

On the basis of the infrared absorption spectra of the square complexes $IrN_2(PPh_3)_2Cl$ and $IrCO(PPh_3)_2Cl$, Collman et al.[88] concluded that molecular nitrogen is a more powerful π-electron acceptor than carbon monoxide. This conclusion is based on the fact that in the formation of the complex the ν(N≡N) stretching vibration frequency falls more than does ν(C≡O) relative to the corresponding vibration frequencies of the gaseous N_2 and CO molecules. Collman et al.[88] do not take into account the fact that in the formation of the CO complex the ν(C≡O) stretching vibration frequency may actually increase, since the upper filled molecular orbital 3σ(CO) is non-bonding (see p. 360).

In fact, in agreement with the qualitative quantum-chemical treatment, carbon monoxide gives rise to stronger σ and π bonds with a transition metal atom than does molecular nitrogen, i.e. CO is a stronger "π-acid" than N_2.

The study of the nitrogen complexes of rhodium(I) and iridium(I)



showed[37] that the ν(M–Cl) stretching vibration frequency is higher by 12–15 cm^{-1} for the *trans*-position with respect to N_2 than for the *trans*-position with respect to CO (Table 10). Since the replacement of the CO molecule by N_2 does not alter the kinematic parameters of the complexes, the masses of molecular nitrogen and carbon monoxide being the same, the difference in the ν(M–Cl) frequencies is undoubtedly due to the difference in the M–Cl bond strengths.

Electron transfer from CO or N_2 via the σ bond to the hybrid ($d_{z^2} + p_z + s$) orbital of the metal hinders the formation of the M–Cl bond (which is the reason for the *trans*-effect).

Dependence of the ν(N≡N) Frequency on the Nature of the Metal

Since the nature of the ligand has a very significant influence on the vibration frequency of the N≡N bond, it is useful to compare the frequencies only for complexes having the same structures and the same ligands. Table 11 lists the values of the ν(N≡N) frequencies for certain nitrogenyl complexes of ruthenium(II), osmium(II), rhodium(I), and iridium(I). Evidently on going from complexes of metals with 4*d* electrons to those of metals with 5*d* electrons, the ν(N≡N) frequency is reduced by 60–90 cm^{-1}, while the ν(M–N_2) frequency is increased by 18 cm^{-1}.

Table 10. Stretching vibration frequencies ν(N≡N), ν(C≡O), and ν(M–Cl) in the square complexes of rhodium(I) and iridium(I)

Compound	ν (N≡N), cm^{-1}	ν (C≡O), cm^{-1}	ν (M–Cl), cm^{-1}
$RhN_2Cl(PPh_3)_2$	2152	—	315
$RhCOCl(PPh_3)_2$	—	1967	304
$IrN_2Cl(PPh_3)_2$	2095	—	329
$IrCOCl(PPh_3)_2$	—	1955	315

Probably the nitrogenyls of the transition elements in the lower periods have a structure close M=N=N, since with increase in the principal quantum number, there is an increase in the overlap of the molecular orbitals and therefore the d_π–p_π interaction is stronger (see p. 367).

Table 11. Dependence of the stretching vibration frequencies ν(N≡N) and ν(M–N) on the nature of the metal

Compound	ν (N≡N), cm^{-1}	ν (M–N_2), cm^{-1}	Compound	ν (N≡N), cm^{-1}
$[RuN_2(NH_3)_5]Cl_2$	2102	500	$RhN_2Cl(PPh_3)_2$	2152
$[OsN_2(NH_3)_5]Cl_2$	2012	518	$IrN_2Cl(PPh_3)_2$	2095

Kinetic studies of the breakdown of nitrogenyl complexes confirm an increase in the strength of the M–N_2 bond on transition to metals in the lower periods. Thus the Os–N_2 bond energy in $[OsN_2(NH_3)_5]^{2+}$ is not less than 39 kcal $mole^{-1}$,[57] while in the corresponding ruthenium cation $D(Ru-N_2)_2 \simeq$ 25 kcal $mole^{-1}$. In the complex $RuN_2Cl_2THF(H_2O)_2$ the energy of the RuN_2 bond amounts to 22 kcal $mole^{-1}$.[95]

Other Results Obtained by Vibrational Spectroscopy

In the infrared spectra of $[OsN_2(NH_3)_5]X_2$ crystals the absorption band corresponding to the ν(N≡N) frequency results from the superposition of a number of components[37,53,54]. Thus in the spectrum of $[OsN_2(NH_3)_5]Cl_2$ the asymmetric band splits into three components: at 2012, 2022, and 2033 cm^{-1}. At the same time the infrared spectra of solutions of the complex in H_2O and D_2O are characterised by a single symmetrical absorption band at a frequency of 2030

cm^{-1}. In the spectra of the corresponding ruthenium complexes, both in the crystalline state and in aqueous solution, there is a single line. The splitting of the $\nu(N\equiv N)$ band of osmium nitrogenyls has been explained[37,54] by the resonance interaction of the translationally non-equivalent molecules in the unit cell of the crystal (the Davydov effect). In view of the splitting, it was concluded that the crystals of osmium nitrogenyls, in contrast to the ruthenium compounds, have a lattice with a lower symmetry than cubic.

In the spectra of the crystalline compounds $FeH_2N_2(PPh_3)_3$ and $FeH_2N_2(PPh_2Et)_3$ the absorption bands corresponding to the N≡N stretching vibrations are split into three components[85] (Fig. 6) which are displaced towards lower frequencies by 65–70 cm^{-1} when $^{14}N_2$ is replaced by $^{15}N_2$. In the spectra of crystals containing a mixture of the isotopic molecules $[FeH_2{}^{14}N^{14}N(PPh_3)_3]$ and $[FeH_2{}^{14}N^{15}N(PPh_3)_3]$ the band corresponding to the isotope present at a low concentration is not split, while that corresponding to the isotope at a high concentration is split.

These results show that the splitting of the infrared band due to the N≡N stretching vibrations is due to the resonance interaction of the translationally non-equivalent molecules in the unit cell of the crystals[86]. Due to the statistical distribution of the isotopic molecules containing nitrogen-28 and nitrogen-29 with different $\nu(N\equiv N)$ vibration frequencies, in the mixed crystals the resonance conditions are not realised and the Davydov components are absent.

The occurrence of Davydov splitting and the presence of three $\nu(N\equiv N)$ components shows that $FeH_2N_2(PPh_3)_3$ and $FeH_2N_2(PPh_2Et)_3$ crystallise with a lattice whose symmetry is lower than cubic and the number of molecules in the unit cell of the crystals is not less than three. Probably this effect can also account for the splitting associated with the stretching vibration of the N≡N bond in the crystalline complex $CoHN_2(PPh_3)_2$ into two components[66] with frequencies of 2101 and 2087 cm^{-1}.

The frequencies of the first and second overtones of the stretching vibration of the N≡N bond in the complex $[OsN_2(NH_3)_5]Br_2$ have been observed[57] at 3998 and 5904 cm^{-1}. The calculated anharmonicity constant X_e of the N≡N bond vibration in the complex is about 0.0125, while for gaseous nitrogen $X_e \simeq 0.0063$. According to an approximate estimate based on the convergence of the vibrational levels, the energy of the NN bond in the complex is about 120 kcal $mole^{-1}$. Unfortunately the accuracy of this estimate is low and the error is unknown. At the same time such a sharp increase of bond energy compared with the nitrogen molecule is not surprising, since the dissociation of the NN bond in the complex should result in the formation of a strong Os≡N bond. The range of values of the M≡N bond energies for various metals in the gas phase is 96–145 kcal $mole^{-1}$.[89] Thus the reduction of the N≡N bond energy in the complex should indeed be appreciable.

Raman Spectra. $\{[Ru(NH_3)_5]_2N_2\}(BF_4)_4$ and $[Ru(NH_3)_5N_2](BF_4)_2$

It has been shown[58] that in the infrared spectrum of the dinuclear complex $\{[Ru(NH_3)_5]_2N_2\}^{4+}$ there is no absorption characteristic of the stretching vibration of the N≡N bond. In view of this finding, a symmetrical structure was postulated[58], in which the N≡N molecule behaves as a bridge ligand.

Study of the Raman spectra of the crystalline tetrafluoroborate salt of this complex[90], containing $^{14}N_2$ and $^{15}N_2$, showed that the spectrum includes intense bands at frequencies of 2100 and 2030 cm^{-1} for the light and heavy nitrogen respectively. Therefore these lines should be assigned to the stretching vibration of the nitrogen–nitrogen bond {belonging to the symmetry type A_{1g}, which is allowed in the Raman spectrum and forbidden in the infrared spectrum [see Fig. 5 and Table 7, structure (III)]} and the order of this bond is close to three.

It should be noted that the formation of the complex with the linear structure Ru–N≡N–Ru leads to a decrease of the vibration frequency of the N≡N bond compared with the mononuclear complex. Thus the Raman spectrum of $[Ru(NH_3)_5N_2](BF_4)_2$ shows an intense line at 2133 cm^{-1}, while in the dinuclear complex the vibration frequency falls to 2100 cm^{-1}.

The Nature of the M–N_2 Bond

Even before the synthesis of the first complexes of molecular nitrogen with transition metal compounds, the question of the possibility of their formation and of the nature of their chemical bond was discussed. Orgel[91] compared transition metal carbonyls with the nitrogenyls, which were hypothetical at the time. According to Orgel, electron transfer from the σ orbital of N_2 to the metal and from the metal to the antibonding π orbital of N_2 leads to the transition of the neutral N_2 molecules to an excited state identical with the highest states of the $n-\pi$ transition. For N_2, the energy of the $n-\pi$ transition is 7.3 eV, while in the case of carbon monoxide the energy is 6 eV, the energies of the $\pi-\pi$ transitions for the two molecules being 6–8 and 7–8 eV respectively. Hence it was concluded that the configuration $M-\overset{N}{\overset{\|}{N}}$ is more favoured compared with M–N≡N than is $M-\overset{C}{\overset{\|}{O}}$ compared with M–C≡O.

However, all the transition metal nitrogenyls known at the present time and also the surface complexes of nitrogen evidently have a linear structure like the carbonyls and diazo-compounds. As already mentioned, this has been established by X-ray diffraction analysis and by infrared and Raman spectroscopy.

Furthermore examination of the experimental data for the nitrogenyl complexes permits the following preliminary generalisations: (1) molecular nitrogen complexes are formed by compounds of transition metals in lower oxidation states, which have unshared pairs of d electrons; (2) the contribution of the $d\pi-p\pi$ interaction is significant in the formation of the M–N_2 bond, N_2 behaving as a π-electron acceptor ligand; (3) donor ligands enhance the stability of molecular nitrogen complexes and π-acceptors reduce it‡; (4) other conditions being equal, the complexes of metals in the lower Periods of the Periodic System are more stable than those in the higher Periods; (5) the nitrogenyl complexes known at the present time are diamagnetic, i.e. stable complexes are probably formed with metals in low-spin states.

‡ This explains the finding that each new N_2 molecule weakens the M–N_2 bond and polynitrogenyl complexes are less stable than mononitrogenyl complexes. We may also note that this distinguishes polynitrogenyls from polycarbonyls, many of which are very stable. Probably this is because carbon monoxide is not only a powerful π-electron acceptor ligand but also a much stronger σ-electron donor than nitrogen (see p. 360). Therefore the introduction of several CO molecules does not alter significantly the electron density at the metal.

We may note that N_2 complexes have been obtained for compounds of ruthenium and osmium [metals in Periods (V) and (VI)] with ligands which give rise to both weak (H_2O, NH_3, C_4H_8O, etc.) and strong (PR_3, H) crystal fields. For metals of Period (IV) (iron, cobalt, and nickel), covalent nitrogenyl complexes have been obtained (and these are probably the most stable) with ligands giving rise to a powerful field. This is evidently because low-spin states of metals of Periods (V) and (VI) are realised with both types of ligand, while for iron, cobalt, and nickel compounds spin-paired states can be obtained only with strong-field ligands.

It is striking that the electron shells of the metals in the complexes $FeH_2N_2(PPh_3)_3$ and $CoHN_2(PPh_3)_3$ are isoelectronic, as in the carbonyls $FeH_2(CO)_4$, $CoH(CO)_4$, and $Ni(CO)_4$, and in the nitrogenyls the number of outer electrons (18) corresponds to an inert gas shell. The number of electrons in $NiN_2[P(C_6H_{11})_3]_2$ is two less, but the complex may also include a solvent molecule with an electron pair.

Probably the stabilising effect of hydride bonds can be explained by the fact that nitrogen is a powerful electron donor. For a carbonyl hydride, this is illustrated by its acid dissociation in solution:

$$CoH(CO)_4 \rightleftarrows H^+ + [Co(CO)_4]^-.$$

We shall now examine the scheme of the molecular orbitals for the cation $[OsN_2(NH_3)_5]^{2+}$ shown in Fig. 8 (for clarity the energy scale has been extended).

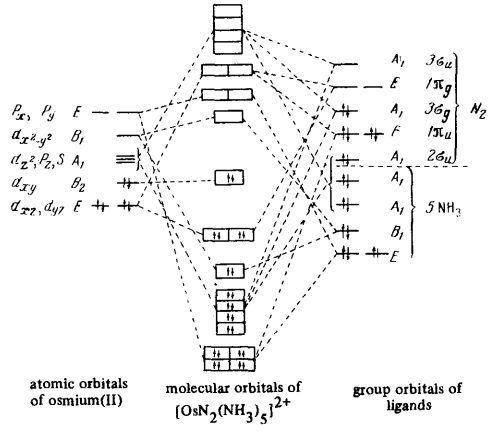


Figure 8. The system of molecular orbitals of $[OsN_2(NH_3)_5]^{2+}$ (arbitrary scale).

The $[OsN_2(NH_3)_5]^{2+}$ cation belongs to the point group C_{4V} and therefore the distribution of the atomic orbitals of osmium(II) corresponds to splitting in a tetragonal field. The ammonia molecules, which are σ-electron donors, are taken into account by the introduction of five groups of σ-orbitals. By taking into account the symmetry and the distribution of the osmium(II) and N_2 levels, it is seen that in the formation of the complex osmium cations there is, on the one hand, electron transfer from the bonding atomic orbitals of osmium of the type $E(d_{XZ}, d_{YZ})$ to the lower antibonding molecular orbital of nitrogen $(1\pi_g)_{XZ,YZ}$ and, on the other hand, the filled molecular orbitals of nitrogen of the type $A_1(3\sigma_g, 2\sigma_u)$ are capable of donating electrons to the antibonding hybrid osmium orbital $(d_{Z^2} + p_Z + s)$.

Fig. 9 gives a conventional representation of these two components of the metal–molecular nitrogen bonds in the complex $[OsN_2(NH_3)_5]^{2+}$ both for a linear and a non-linear configuration of the fragment. Fig. 9 shows that the overlapping of the orbitals is greater for the linear configuration of the $Os-N_2$ fragment, since in this case a dative bond is formed as a result of the overlapping of two pairs of orbitals, $d_{XZ}-(1\pi_g)_{XZ}$ and $d_{YZ}-(1\pi_g)_{YZ}$ in the mutually perpendicular planes xz and yz. In the π-complex with C_{2V} symmetry both dative and donor–acceptor interaction is less intense due to the smaller degree of overlapping of the orbitals.

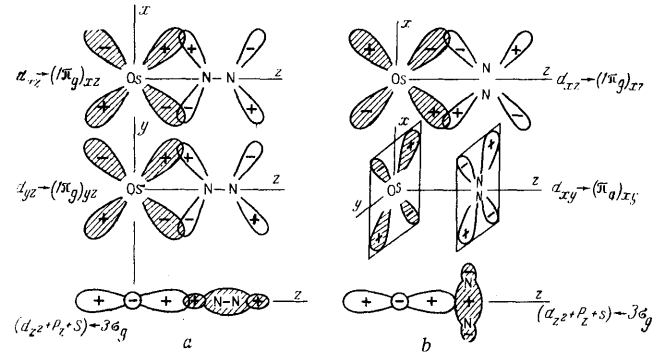


Figure 9. The overlapping of molecular orbitals in $[OsN_2(NH_3)_5]^{2+}$: *a*) for the linear coordination of molecular nitrogen, i.e. Os–N≡N (C_{4V}); *b*) for the π-complex (C_{2V}).

According to the principle of overlapping and orientation, the complex has the structure in which the overlap integrals are a maximum. Therefore it is evident that the complex with C_{4V} symmetry should be more stable than the complex with C_{2V} symmetry.

The hypothetical $Fe-N_2$ fragment, consisting of a neutral iron atom and a coordinated nitrogen molecule, has been examined quantum-chemically[92] for the two possible structures Fe–N≡N and Fe–$\overset{N}{\underset{N}{\|}}$. On the basis of the calculation, it was concluded[92] that the linear coordination of nitrogen is to be preferred and the charge distribution for the Fe–N′≡N″ model was obtained (Table 12). In this calculation the orbital energies calculated by the Hartree–Fock–Roothaan method were used as the diagonal elements of the effective Hamiltonian. As a result, the N_2 molecule was found to have an overall positive charge, i.e. nitrogen behaves as a donor in relation to the metal atom.

If the diagonal elements are approximated by the ionisation potentials of the valence states[93], one obtains for the linear model M–N′≡N″ (where M = Fe or Ru) a different charge distribution (Table 12), which agrees qualitatively with the experimental data concerning the π-electron acceptor properties of N_2 as a ligand.

Population analysis of the M–N and N–N bonds shows[93] that the contribution of the π-electron component to the metal–nitrogen bond is greater than that of the σ-electron

component, and the σ-components of the nitrogen–nitrogen bond in the coordinated and free N_2 molecules are almost indistinguishable. (The population of the bond may serve to some extent as a characteristic of its strength.)

Table 12. The atomic charges and electron populations for the fragment M–N′≡N″

Compound	Population of M–N′ bond		Population of N′–N″ bond		Atomic charges			Refs.
	σ-component	π-component	σ-component	π-component	M	N′	N″	
Fe—N′≡N″	0.433	0.254	0.845	0.746	—0.43	1.01	—0.58	92
	0.215	0.302	0.829	0.561	0.485	—0.188	—0.297	93
Ru—N′≡N″	0.255	0.313	0.832	0.590	0.426	—0.150	—0.276	93
N≡N			0.785	0.875				93

* The interatomic distances (Å) used in the calculation by Vinogradova et al.[93] were as follows: $r(Fe–N) = 1.8$; $r(N–N) = 1.16$; $r(Ru–N) = 1.9$.

3. THE MECHANISM OF THE FORMATION OF MOLECULAR NITROGEN COMPLEXES

Nitrogen is still an unusual ligand in the chemistry of coordination compounds and therefore it is interesting to examine how it becomes coordinated. There are very few data on this problem. The mechanism of the interaction of nitrogen in the reduction of $RuCl_3.nH_2O$ in tetrahydrofuran has been investigated in greatest detail[94,95]. As already stated, the main product of this reaction is $RuN_2Cl_2(H_2O)_2THF$; a certain amount of $RuN_2Cl_2(H_2O)_3$ is also formed. The study of the reaction kinetics led to the conclusion that nitrogen reacts with the coordination-unsaturated species RuL_5 formed as an intermediate in the reduction. The RuL_5 species may be coordinated not only to nitrogen but also to any other compound L′ present in the solution. For example, L′ may be water. The dependence of the yield of the nitrogenyl complex on nitrogen pressure is consistent with the mechanism

$$RuCl_3 \cdot nH_2O \xrightarrow{Zn} RuCl_2L_3$$

$$RuCl_2L_3 \begin{cases} \xrightarrow[N_2]{k_2} RuN_2Cl_2L_3, \\ \xrightarrow[L']{k_3} RuCl_2L_3L'. \end{cases}$$

The study of the exchange of molecular nitrogen with the nitrogen in the coordination sphere of ruthenium nitrogenyls[94,95] confirmed that nitrogen interacts with the coordination-unsaturated species RuL_5. It was established that the exchange of molecular nitrogen involves substitution by a dissociative mechanism of S_N1 type:

$$\begin{gathered} RuN_2L_5 \underset{k_2}{\overset{k_1}{\rightleftarrows}} RuL_5 + N_2, \\ RuL_5 + L' \xrightarrow{k_3} RuL_5L'. \end{gathered} \qquad (1)$$

In accordance with this mechanism, the exchange reaction takes place only in the thermal decomposition of the nitrogenyl complex. The application of the method of steady-states to mechanism (1) leads to the following expression for the rate of decomposition:

$$\frac{dz}{dt} = \frac{k_1k_2(a-z)L'}{k_2N_2 + k_3L'} = k_{eff}(a-z) \qquad (2)$$

where $z = [RuL_5L']$ and a is the initial $[RuN_2L_5]$. According to Eqn. (2), the decomposition of the nitrogenyl complex in an atmosphere of nitrogen is a first-order reaction, $1/k_{eff}$ varying linearly with the nitrogen pressure. The addition of water slows down the nitrogen exchange in the complex. It is reasonable to conclude that water competes with nitrogen in the reaction with RuL_5. The ratio of the rate constants (k_2/k_3) for the reactions of N_2 and H_2O with RuL_5 was determined from the kinetic data. The ratio is independent of temperature and equal to about 3.1. Tetrahydrofuran competes much less strongly than water. The results suggest that the difference in the reactivities of nitrogen and water is determined mainly by steric factors and the activation energy for the reaction of N_2 with RuL_5 is close to zero. Thus it has been shown[94,95] that nitrogen is coordinated only by a dissociative mechanism (S_N1) and not by an S_N2 mechanism (in contrast, for example, to the coordination of carbon monoxide) and that the rate constant for the reaction with a coordination-unsaturated compound is very high.

It may be supposed that the coordination of nitrogen in the reaction

$$[Ru(NH_3)_5H_2O]^{2+} + N_2 \rightarrow [RuN_2(NH_3)_5]^{2+} + H_2O$$

in aqueous solution at atmospheric nitrogen pressure[41] takes place by a similar mechanism. The kinetics of this reaction have been investigated recently[96] and the rate constants for the formation of the mono- and di-nuclear pentammineruthenium nitrogenyls have been measured, but the possibility of a dissociative mechanism was not discussed at all. Nevertheless it may be supposed that the water molecule in the aquopentammine-complex is weakly bound to the ruthenium atom and the following equilibrium exists in aqueous solution:

$$[Ru(NH_3)_5H_2O]^{2+} \rightleftarrows [Ru(NH_3)_5]^{2+} + H_2O$$

and the $[Ru(NH_3)_5]^{2+}$ ion interacts with molecular nitrogen.

Sacco and Aresta[59] obtained the complex $FeH_2N_2L_3$ (where $L = PPh_2Et$) in the reaction of N_2 with the iron dihydride compound FeH_2L_3. It was noted that the complex is formed readily not only in solution but also in the solid state. Here too nitrogen probably adds to the five-coordinated iron compound FeH_2L_3, which, however, is stable in this case. Further studies should show how general is the conclusion that nitrogen is incapable of reacting by an S_N2 mechanism.

4. COMPLEXES OF MOLECULAR NITROGEN AS INTERMEDIATES IN REDUCTIVE NITROGEN FIXATION

Several types of nitrogen reduction reactions with formation of ammonia or its derivatives are known at present.

The Formation of Nitrides in the Reaction of Nitrogen with Metals

Metals usually react with nitrogen at a high temperature; even lithium and the alkaline earth metals (calcium, strontium, and barium), which are known to form nitrides at room temperatures, react extensively with nitrogen only on heating. In many cases the necessity for severe reaction conditions is probably not due so much to the inertness of nitrogen as to the formation on the surface of oxide, nitride, etc. films; on clean surfaces nitrogen reacts with the metal at a high rate. Thus, if the reaction of lithium with ethyl bromide is carried out in nitrogen, the excess of lithium is converted into the nitride[97] at 30°C. Studies on the chemisorption of nitrogen on tungsten[27] and molybdenum[98] show that nitrogen is atomised (i.e. evidently forms surface nitrides) at a low temperature.

Heterogeneous-Catalytic Hydrogenation of Nitrogen

This process, which has been known for a long time and is widely used in technology, is carried out under comparatively severe conditions in the presence of metals such as iron, ruthenium, and osmium. Without considering this process in detail, to which numerous monographs and reviews have been devoted (see, for example, Kiperman[99]), we may note that for this process too the state of the catalyst surface is very important: on a clean iron surface, the synthesis of ammonia[100] takes place even at 80°C, albeit slowly.

Reduction of Nitrogen in Solutions

In 1964 Vol'pin and Shur[101] discovered a new nitrogen reduction reaction in hydrocarbon and ethereal solutions under the action of reducing agents such as organometallic compounds, metal hydrides, and metals [C_2H_5MgBr, Mg + MgI_2, C_6H_5Li, Al(iso-Bu)$_3$, etc.] in the presence of transition metal derivatives [$TiCl_4$, $(C_2H_5)_2TiCl_2$, $FeCl_3$, VCl_4, etc.]. A large number of examples of this reaction were subsequently observed in several studies[102,103].

The reaction takes place under very mild conditions, for example at room temperature and atmospheric nitrogen pressure. The reaction products yield ammonia on hydrolysis[101] and are probably nitride derivatives[104], although in most cases their structure is still unknown. It is interesting that in some cases the hydrolysis results also in the formation of aromatic amines[102]. Usually the yield of ammonia after the hydrolysis of the reaction products is smaller than or close to the stoichiometric value when calculated relative to the transition metal but titanium tetrachloride is a catalyst for the formation of aluminium nitride[105] (at least in the system Al–$AlBr_3$–$TiCl_4$).

In an attempt to simulate the biological fixation of molecular nitrogen, various workers investigated the reduction of nitrogen in aqueous solutions by powerful reducing agents in the presence of transition metal compounds, and some of them reported[106-108] the formation of small amounts of ammonia. These results could not, however, be reproduced[109].

Enzymic Fixation of Molecular Nitrogen

This extremely important biological process is carried out by many micro-organisms. Recently the mechanism of this reaction has been vigorously investigated and particularly important results have been obtained after the successful isolation of active cell-free extracts from the nitrogen-fixing bacteria. Without going into the details of these investigations (see the appropriate reviews[110,111]), we may note the following principal features of the mechanism of the biological fixation of nitrogen: (1) the reaction constitutes the reduction of nitrogen with intermediate formation of ammonia; (2) the enzymic system consists of two main components; one of them activates the nitrogen molecule and the other is responsible for electron (or hydrogen atom) transfer to the activated nitrogen molecule; metal atoms (iron and molybdenum) participate in both these processes; adenosinetriphosphoric acid, which is converted into adenosinediphosphoric acid and phosphate during the reaction, also plays an important role; (4) the part of the enzymic system activating the nitrogen is deactivated by carbon monoxide and hydrogen.

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Bearing in mind that metals or their compounds participate in all nitrogen reduction reactions, it is reasonable to suppose that the first stage involves the formation of an N_2 complex with the metal. In some of the earlier studies[15,29,101,112,113,114] it was also believed that the formation of a nitrogen complex is an essential intermediate stage in nitrogen fixation. The discovery of nitrogen complexes and the study of the complex-formation reactions have confirmed this view. Indeed, one may note in the first place that systems in which N_2 complexes are formed resemble those in which nitrogen is hydrogenated or reduced.

In many cases nitrogen complexes with ruthenium, osmium, cobalt, and iron compounds are formed in solution under the same conditions and under the action of the same reagents as the nitride derivatives in the reduction of nitrogen. Some examples are presented in Table 13.

Table 13. Examples of systems in which different products are formed with N_2

System	Nitrogen-containing product	Refs.
$RuCl_3$+EtMgBr+N_2	nitrogen complex	43
$FeCl_3$+EtMgBr+N_2	nitride derivative	95
Co (acac)$_3$+$AlEt_2OEt$+PPh_3+N_2	nitrogen complex	60—62
Ni (acac)$_3$+Al (iso-C_4H_9)$_3$ + N_2	nitride derivative	119

Ruthenium(II) complexes are formed in an aqueous medium and in the presence of oxygen, which explains why water is not an inhibitor of the biological fixation of nitrogen. Further reduction of nitrogen in the complexes formed in the first stage may consist in the formation of an "azo-complex" with two metal atoms:

$$M' + N_2 \rightarrow M'-N\equiv N,$$
$$M'-N\equiv N + M'' \rightarrow M'-N=N-M''.$$

The double bond –N=N– is further reduced to ammonia derivatives. A model for this mechanism of the biological fixation of nitrogen was proposed by Parshall[112], who considered the reduction of diazo-compounds (as analogues of the nitrogen molecule in the complex) in the presence of a hydride derivative of divalent platinum.

However, the formation of complexes is not a sufficient condition for the activation of nitrogen for further reactions. Indeed, the known nitrogenyl complexes are very stable with respect to nitrogen reduction reactions in the coordination sphere of the metal. As already pointed out, the reports[38,39] of the reduction of nitrogen in the ruthenium complex under the action of sodium borohydride were not subsequently confirmed[40].

In other nitrogenyl complexes nitrogen is also not reduced under the action of the usual reducing agents[46,47]. It can of course be supposed that the intermediate complexes in the reduction of nitrogen differ in structure from the stable nitrogenyls; for example, they could have the structure of the π-complex type $M-\overset{N}{\underset{N}{\|}}$. However, it is more likely that the reason lies in the necessity for a definite combination of properties in the metals comprising the complexes in order that the catalytic process may take place.

To establish what complexes can be intermediate in the catalytic reduction of nitrogen, it is necessary to bear in mind the exceptional stability of the first bond dissociated in the N_2 molecule (about 130 kcal mole^{-1}) and, on the other hand, the instability of the remaining two bonds. The addition of one H_2 molecule to a nitrogen molecule with formation of the di-imide N_2H_2 is endothermic to the extent of 49 kcal mole^{-1},[115] whereas the hydrogenation of acetylene to ethylene, for example, takes place with the evolution of 42 kcal mole^{-1}. Therefore the hydrogenation of nitrogen via the intermediate formation of free N_2H_2 is impossible under mild conditions. For this reason, the reaction involving "incorporation" in the M–H bond is unlikely for nitrogen:

$$M{-}H + N_2 \rightarrow M{-}N{=}N{-}H$$

This could be regarded as two-electron reduction (such a reaction might be put forward by analogy with the hydrogenation of acetylenes and olefins). Hence it is not surprising that nitrogen is not hydrogenated on the usual catalysts active in the hydrogenation of other unsaturated compounds.

In order to reconcile the ease of reduction of nitrogen in biological systems with the apparent necessity for the intermediate formation of di-imide (or its derivative), it has been suggested[116] that the formation of N_2H_2 is accompanied by a coupled reaction involving an energy gain, so that the overall free energy of the reaction decreases and the formation of N_2H_2 becomes possible.

However, in the formation of nitrogen complexes with transition elements there is a possibility, in principle, of another reduction pathway, not involving intermediate compounds with an N=N double bond.

In mono- and di-nuclear nitrogenyl complexes the order of the bond between the nitrogen atoms remains close to three. If the dinuclear complex is now acted upon by a two-electron reducing agent X_2, then two bonds in the nitrogen fragment may dissociate at once with formation of a hydrazine derivative as a result of the additional transfer of two electrons from the metal atoms constituting the complex:

$$M'\cdots N{\equiv}N\cdots M'' + X_2 \rightarrow \begin{matrix} & X & X & \\ & \diagdown & \diagup & \\ M' & & N{-}N & M'' \end{matrix}$$

Thus the intermediate formation of a dinuclear complex with molecules of nitrogen subsequently allows the four-electron reduction to a hydrazine derivative in one stage§.

The overall addition of two H_2 molecules to N_2 with formation of hydrazine in aqueous solution is endothermic only to the extent of 8 kcal mole^{-1}. Reducing agents only a little stronger than H_2, for example sodium dithionate, are capable of providing sufficient energy for the reduction of nitrogen to hydrazine or its derivatives. It is then necessary to remember that the metals comprising the complex must themselves be relatively powerful one-electron reducing agents. Furthermore, the complexes must not be too stable, since an increase in bond strength in the complex corresponds to a greater energy expenditure in its subsequent reduction.

In Vol'pin–Shur reactions these conditions are evidently fulfilled. Indeed in the presence of powerful reducing agents such as aluminium, RMgX, LiR, etc. transition metal compounds are reduced to low states of oxidation, becoming fairly powerful reducing agents. Since intermediate nitrogen complexes have not been detected in these reactions so far, their stability is probably low.

From this standpoint, it is not surprising that stable N_2 complexes of ruthenium, osmium, etc. cannot be reduced. The $M{-}N_2$ dissociation energy in these complexes reaches tens of kcal mole^{-1} and the capacity for electron transfer is low: osmium(II) and ruthenium(II) in these compounds are weaker reducing agents than H_2.

On the basis of the above considerations alone, three cases of the interaction of a metal or its compound (M) with an N_2 molecule have been examined[117]:

1. M is a very powerful reducing agent capable of transferring an electron to the N_2 molecule or forming a covalent bond by complete dissociation of one of the bonds in the nitrogen molecule in the absence of d_π–p_π interaction. The reduction potential of M in such a reaction must be not less than 2.5 eV. Even atomic hydrogen does not react with nitrogen, since the energy of the $H{-}N_2$ bond is negative. It may be supposed that a reaction of this kind takes place with lithium and certain other metals. Further addition of M to $M{-}N_2$ will occur very readily with the final formation of a nitride. At low temperatures M cannot be a catalyst for a reducing agent weaker than itself (for example H_2), since this would necessitate the expenditure of a large amount of energy on the dissociation of the M–N bond in the nitride. The reaction is of course impossible in an aqueous medium.

2. M is a weak reducing agent. The bond with nitrogen is formed mainly as a result of d_π–p_π interaction; the bond order in N_2 remains close to three. The formation of ruthenium(II) and osmium(II) complexes probably approaches this type. These complexes and the dinuclear complexes $M'N_2M''$ are formed readily but further reduction of nitrogen requires the use of a reducing agent almost as strong as for free nitrogen. The reaction largely terminates with formation of complexes stable to reduction.

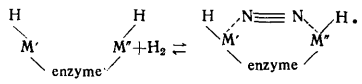
3. The intermediate case. The energy of the formation of the complexes M'N and $M'N_2M''$ includes a considerable contribution from d_π–p_π interaction, and at the same time M and M'' are comparatively powerful reducing agents capable of transferring one electron to an acceptor molecule. It is in fact in this case that we have the possibility of catalysis in the presence of M' and M'' of the reduction of molecular nitrogen by a reducing agent more powerful than M' and M'', although the reaction may of course terminate with formation of nitrides containing the M' and M'' atoms. The Vol'pin–Shur reaction and heterogeneous hydrogenation may be assigned to this case.

When a reducing agent active in an aqueous medium (of the type of sodium hydrosulphite) and with a reduction potential of about −0.2 eV is employed, the catalytic reaction can be achieved only for definite values of the reduction potential of M' and M'' and for definite strengths of the N_2–catalyst bond in the complex. These conditions are probably realised in the biological fixation of nitrogen, where M' and M'' are respectively both Fe atoms or Fe and Mo atoms present as constituents of the enzymes and forming a dinuclear complex with nitrogen in the course of fixation. It may be supposed[58] that the role of ATP in nitrogen fixation consists in its participation in the formation of hydride derivatives of molybdenum or iron.

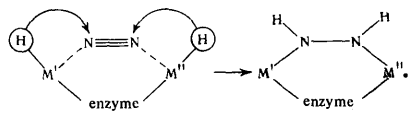
There are grounds for believing that in the biological fixation of nitrogen cyclic complexes with molybdenum and iron atoms linked by the enzyme molecule are formed, in contrast to the familiar "azo-complexes". Because of the

§ In principle one cannot exclude the possibility also of the six-electron reduction $M'\ldots N{\equiv}N\ldots M'' + X_2 \rightarrow M'{=}N{-}X + X{-}N{=}M''$. However, such a reaction, which cannot be regarded as a single elementary process, appears to be less likely.

more favourable entropy factor, this should lead to a higher concentration of the intermediate "azo-complex" and a correspondingly higher rate of reaction than in the case of the linear complex:



Further four-electron reduction can be readily represented, for example, as double "incorporation" in the M–H bond:



The formation of *cis*-dideuterioethylene[118] in the reduction of acetylene by the enzymic nitrogen-fixing system in D_2O provides indirect confirmation of the cyclic structure of the intermediate complex.

Further studies will show to what extent this hypothesis is correct.

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As already stated, nitrogenyl complexes with the compounds of seven metals of Group VIII of the Periodic System (iron, ruthenium, osmium, cobalt, rhodium, iridium, and nickel) have been isolated and characterised at the present time. There is no doubt that other transition metals are also capable of forming complexes with N_2 in a low-valence state. Although it may be supposed that the chemistry of nitrogenyls will prove to be less elaborate than the chemistry of the related more stable carbonyls, it will evidently undergo much further development. Probably it will be possible to isolate stable nitrogenyls of many metals (for example, platinum compounds), but unstable complexes with a low heat of formation, which can be observed at a low temperature and a high nitrogen pressure, will prove even more numerous.

The problem of the structure of the complexes is very interesting: it is still obscure whether we are dealing with π-complexes of N_2 or compounds with a structure analogous to that of the carbonyl bridge compound $\begin{matrix} M \\ N\equiv N \\ M \end{matrix}$, etc.

So far very little is known about dinuclear complexes of the type M–N≡N–M, which are of particular interest as possible intermediates in nitrogen reduction reactions. The mechanism of such reactions still requires serious revision and development. Evidently, it is possible to bind N_2 catalytically via unstable complexes (possibly by a process of the type of biological nitrogen fixation) or to synthesise other nitrogen-containing compounds (except ammonia).

It may be hoped that the development of the low-temperature chemistry of molecular nitrogen will lead to the creation of new highly effective catalytic systems and will thereby give rise to the discovery of new industrial methods for the binding of atmospheric nitrogen.

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Branch of the Institute of Chemical Physics,
USSR Academy of Sciences

U.D.C. 546.221

Reactivity of Sulphides

I.S.Chaus and I.A.Sheka

The characteristic features of the interaction of metal sulphides in sintering, fusion, and coprecipitation from their solutions are discussed in this review. It is shown that the formation of solid substitutional solutions at elevated temperatures is due to the similarity of the effective radii of the metals, determined taking into account the degree of covalence of the M-S bond. It has been found that, as the composition of the reacting sulphides becomes more complicated, their miscibility increases and that the greater the similarity of the ionic radii of the metals the easier the formation of solid solutions of the sulphides when the latter are coprecipitated from solution. The bibliography incorporates 213 references.

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I. INTRODUCTION

Sulphides have been attracting the attention of inorganic and analytical chemists for a long time because their low solubility and in most cases a characteristic colour make them suitable for qualitative and quantitative analyses. However, more thorough investigation of the conditions for their isolation from complex solutions and also of the properties of the pure sulphides synthesised showed that changes in the acidity of the solution, which is the decisive factor in their precipitation, is insufficient for quantitative separation. The attempts to prevent coprecipitation by adding to the solution before precipitation various organic and inorganic complex-forming agents were unsuccessful in most cases. The interest in sulphides in the last decade is due to the fact that they, and chalcogenides in general, have semiconductor properties[1-5] and, since their melting points are high, they can be successfully employed up to 800–900°C. Their high stability to thermal dissociation at elevated temperatures in the absence of oxidising agents makes it possible to employ sulphides as constructional materials in the preparation of pure substances.

The vigorous development of the rare-metals industry, which is based mainly on the processing of polymetallic sulphide ores, also requires a more complete study of the chemical behaviour of sulphides.

The reason for the high reactivity of sulphides probably consists in the fact that for most sulphides the heat of the atomisation of sulphur is much higher than that of the metal and therefore polymers are frequently formed[6-8]. The positive electronegativity difference indicates the polarisation of the sulphide sulphur[8,9], which should also enhance the reactivity of the sulphides.

The interaction of these compounds is complicated by the presence in them of three types of bond: covalent, metallic, and ionic. The considerable ionic character of the bonds is typical for the sulphides of alkali and alkaline earth metals and lanthanides. The bonds in the sulphides of B group metals are covalent and those in the transition metal sulphides are of the covalent-metallic type[2,3,6,10-12].

The structures of the crystalline sulphides are various but most of them are highly symmetrical with close packing of the sulphide sulphur or the metal[13,14]. It has been noted[14] that structures of this type are deficient in the metal.

Furthermore, many sulphides tend to form two or more polymorphic modifications, the stability of which is determined not only by the temperature but also by the presence of another sulphide (sometimes even in insignificant amounts).

Thus the reactivity of sulphides should depend on the nature of the bond, the type of lattice, the dimensions of the atoms or ions of the metals whose compounds interact, and their polarising capacity.

It has now been established that sulphides interact with formation of solid solutions and complex sulphides. Nevertheless, so far there is no information which would make it possible to predict the nature of the interaction of simple sulphides.

II. INTERACTION OF SULPHIDES AT ELEVATED TEMPERATURES

1. The Formation of Solid Solutions

According to general hypotheses, the formation of solid solutions of metals or chemical compounds is observed when the crystals belong to the same or similar structural types, when the difference between the lattice constants and the radii of the interacting atoms are small, and when the chemical properties of the metals or the types of chemical bonds are also similar[15]. The failure of any one of the above conditions leads to the formation of a narrow range of solid solutions or their complete absence.

In their interpretation of experimental results, investigators usually compare either atomic or ionic radii (depending on the data obtained), without taking into account as a rule the type of bond. Thus Flahaut et al.[14] based their discussion of data for the formation of the solid solutions of the sulphides of aluminium, gallium, and indium, on the one hand, and magnesium, manganese, zinc, and cadmium, on the other, on the similarity of the atomic radii, and for the sulphides of the lanthanides and magnesium, the calcium subgroup metals, manganese, and lead on the similarity of the ionic radii. However, the bond in lanthanide sesquisulphides[16,17], and in the majority of sulphides in general, has considerable covalent character.

Table 1, which lists the available information about the existence of solid solutions in sulphide systems, shows that the difference between atomic radii cannot account for the formation of the more extensive region of solid solutions of gallium sulphide with Cu_2S than for the corresponding solid solutions with Ag_2S. This applies equally to the systems Cu_2S–Ag_2S, Ga_2S_3–MnS, etc. On the other hand,

germanium and tin sulphides form a continuous series of solid solutions, other conditions being equal. The above examples show that, using atomic or ionic radii alone, it is impossible to account for the presence or absence of a solid solution in the given system.

Table 1. Regions of existence of solid solutions in sulphide systems.

System	Difference between radii,%			Solubility, mole %	Type of lattice of solid solution	Refs.
	ionic	atomic	effective			
B_2S_3—BeS	41.2	19.4	—	nil	—	14
B_2S_3—MgS	74.4	43.1	—	nil	—	14
B_2S_3—ZnS	76.0	34.5	—	nil	—	14
B_2S_3—CdS	80.6	41.7	—	nil	—	14
Al_2S_3—Cu_2S	40.6	10.5	15.3	nil	—	18
Al_2S_3—Ag_2S	50.0	0.7	25.8	nil	—	18
Al_2S_3—MgS	27.0	10.6	9.8	nil on MgS side	—	14
Al_2S_3—ZnS	31.3	7.0	10.3	0–49.9 at.% Al	wurtzite	14
Al_2S_3—CdS	44.6	4.0	23.4	nil on CdS side	—	14
Al_2S_3—MnS	37.4	8.4	12.1	nil on MnS side	—	14
Ga_2S_3—Cu_2S	35.4	8.0	3.5	30 (Cu_2S)	cubic	18
Ga_2S_3—Ag_2S	45.1	3.5	9.8	15 (Ag_2S)	cubic	20
Ga_2S_3—MgS	20.5	13.1	8.8	up to 12 (MgS)	wurtzite	14
Ga_2S_3—ZnS	25.3	4.3	4.1	0–20 and 70–90 90–100 (ZnS)	cubic wurtzite	14, 19
Ga_2S_3—CdS	40.0	7.0	7.0	up to 16 (CdS)	wurtzite	14, 19
Ga_2S_3—MnS	31.2	6.0	6.5	up to 16 (MnS)	wurtzite	14
In_2S_3—Cu_2S	4.2	18.0	—	less than with Ga_2S_3	—	18
In_2S_3—Ag_2S	19.0	8.3	—	ditto	—	18
Y_2S_3—MgS	26.0	11.1	—	up to 23 (Y_2S_3)	cubic	14, 20 21
Y_2S_3—CaS	0.0	8.6	—	up to 5 (Y_2S_3)	cubic	14, 20 21, 22
Y_2S_3—SrS	16.3	16.5	—	very narrow range if any	—	14, 20
Y_2S_3—BaS	20.0	26.0	—	nil	—	14, 20
Y_2S_3—MnS	14.1	27.2	—	up to 23 (Y_2S_3)	cubic	14, 20, 21
Y_2S_3—PbS	20.0	3.3	—	up to 5 (Y_2S_3)	cubic	21
Cu_2S—Ag_2S	15.0	11.0	13.0	nil	—	23, 24
ZnS—MnS	7.7	1.5	2.0	0–52 (MnS)	hexagonal	25
CdS—MnS	11.6	10.7	12.9	continuous series	hexagonal	
Ag_2S—PbS	14.4	17.2	—	0.4 (Ag_2S at 700°C) 3.0 (PbS at 605°C)	—	26
Ag_2S—Bi_2S_3	3.0	20.9	—	4.0 (Bi_2S_3 at 615°C)	—	26
PbS—Bi_2S_3	9.1	4.4	—	9 (Bi_2S_3 at 800°C) 3 (Bi_2S_3 at 400°C)	—	26
GeS—SnS	4.0	11.4	—	continuous series	ortho-rhombic	27
ZnS—FeS	4.5	0.0	6.8	up to 16 (FeS)		28
FeS—($TiS \cdot TiS_2$)	12.4	16.9	4.7		NiAs, CdI_2 type	29
CoS—($TiS \cdot TiS_2$)	13.8	15.9	11.1		CdI_2 type	29
NiS—($TiS \cdot TiS_2$)	14.5	11.5	14.2		CdI_2 type	29

Therefore it is difficult to agree with the statement [14, 20] that the occurrence of a wide range of solid solutions is possible in systems where the ionic radii of the metals differ by 27–28%.

The presence of a covalent bond should reduce the miscibility of sulphides, since this entails the mutual substitution not of metal atoms or ions but of groups of the type $M_xS_y^{n(\pm)}$. However, since sulphide sulphur tends to form its own lattice, it may be supposed that in its formation the sulphur incorporated in a species of the type $M_xS_y^{n(\pm)}$ can also serve as a "constructional material". Therefore formally the dimensions of this species may be described by the radius of the metal.

The determination of the effective charges of the elements in sulphides showed that the ionic character of the bond differs appreciably for various metals and lies in the range 30–60%. [6,12] This value is fairly appreciable in calculations designed to establish the similarity of ionic or atomic radii of metals and therefore a correction allowing for it must be introduced. Hence we calculated "effective" radii (Table 2) defined as the sum

$$\frac{q \cdot r_{M^{n+}}}{n} + \left(1 - \frac{q}{n} \cdot r_{M\cdot}\right)$$

where n is the valence of the metal, q its effective charge in the sulphide, and $r_{M\cdot}$ and $r_{M^{n(\pm)}}$ are the atomic or ionic radii.

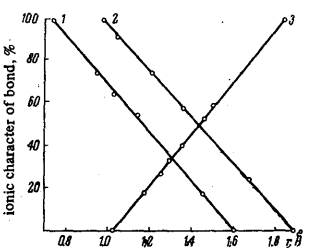
The validity of the calculations is confirmed by the fact that the calculated effective radii for both the cations and sulphide sulphur lie satisfactorily on the straight line drawn through the values of the ionic and atomic radii (Figure).

Table 2. "Effective" radii of metals in sulphides.

Sulphide	Effective radius, Å	Sulphide	Effective radius, Å	Sulphide	Effective radius, Å
Cu_2S	1.18	BaS	1.95	FeS	1.06
Ag_2S	1.35	ZnS	1.16	CoS	1.12
MgS	1.11	CdS	1.31	NiS	1.09
CaS	1.47	MnS	1.14	Al_2S_3	1.00
				Ga_2S_3	1.22

Comparison of the metal radii obtained in this way with the experimental values for gallium in Ga_2S_3 shows (Table 1) that they differ by not more than 9.8%. The following series of compounds with increasing size of the region of solid solutions of gallium sulphide with certain metal sulphides has been constructed on the basis of the calculated data: $Cu_2S > ZnS > MnS > CdS > MgS > Ag_2S$; it agrees satisfactorily with the experimental series [14,18,19]:

$$Cu_2S > ZnS > MnS \geqslant CdS \geqslant Ag_2S > MgS$$



Variation of the effective radius with the ionic character of the bond for sodium (curve *1*), magnesium (curve *2*), and sulphur (curve *3*) in their compounds.

Some deviation observed in the case of Ag_2S is evidently due to the fact that the range of existence of the solid solution in this system has been established only approximately. We believe that the solubility of Ag_2S in Ga_2S_3 should be less than 12 mole %.

The above hypothesis agrees well with the results of studies on systems consisting of FeS, CoS, NiS, and TiS. $.TiS_2$, [29] where the empirical series based on the range of existence of solid solutions—FeS ≫ CoS > NiS—agrees with the series based on the difference between the effective radii of the metals (Table 1). The calculation of the radii was made on the basis of the titanium radius in TiS, which is of decisive importance in this case. The sulphides CrS, VS, and MnS are even less capable of forming solid solutions with $TiS.TiS_2$.

Because of the lack of data on the effective charges of the metal and sulphur in lanthanide sesquisulphides, it is unfortunately impossible to make a similar comparison for their interaction woth the sulphides of magnesium, manganese, lead, and calcium subgroup metals[14,20,21]. However, the available effective charges for the latter compounds explain why in the experimental series based on the size of the solid solution regions–MgS > MnS > CaS > PbS > SrS > BaS–manganese sulphide occupies an intermediate position and strontium and barium sulphides altogether fail to form solid solutions or the solid solutions are formed only over a narrow range.

The introduction of the concept of the "effective" radius of the metals in sulphides permits the elimination of the contradictions existing in the literature. As an example, one may quote the data of Flahaut and coworkers[20], who failed to explain why the solid solution region in the systems Y_2S_3–MgS or Y_2S_3–MnS is greater than in the system Y_2S_3–CaS, although the ionic radii of calcium and yttrium are almost the same.

It is noteworthy that sulphide sulphur forms a close-packed sublattice with octahedral and tetrahedral vacancies, which are occupied by metals in a definite sequence. Since the dimensions of these sites are smaller than those of the majority of metals, a polarisation effect occurs when the vacancies are filled. Analysis of the data obtained shows that the formation of solid solutions should be most complete when the high symmetry of the crystals is further increased or maintained. This inturn is possible when the dimensions of the metals undergoing mutual substitution and the bond types are similar. Indeed the solid solutions obtained in the vast majority of cases crystallise in the cubic or hexagonal system (Table 1). The high symmetry of the crystals in the formation of solid solutions is also due to the tendency of the sulphide sulphur to give rise to its own intrinsic sub-lattice. Therefore the factors leading to its distortion alter the energy of the crystal, in consequence of which it becomes less stable. Conversely, if the addition of another sulphide favours the formation of an undistorted sulphur sublattice, miscibility is observed even when the initial substances differ considerably in symmetry type. As an example, one may quote the studies of Hahn et al.[18], who observed that the addition of small amounts of copper or silver sulphide stabilises the zinc blende structure, which is unstable for gallium sulphide at 900°C. An exception is the system GeS–SnS in which a continuous series of solid solutions is formed. However, X-ray diffraction studies showed that these sulphides form two types of solid solutions, on the basis of GeS and SnS.[27]

Since the nature of the chemical bond in sulphides is variable, the charges of the metal and sulphur should alter on formation of solid solutions. This favours an increase or decrease of the covalent character of the bond and a simultaneous deviation of the metal radii from those in the initial compounds. These changes are small, since mixed crystals are formed only when the type of chemical bond and dimensions of the metals in the initial sulphides are similar. Indeed, when aluminium sulphide is added to zinc sulphide, the Al–S interatomic distance decreases, while in the systems MS–L_2S_3 (L = lanthanide) the L–S distance increases. In the first example the addition of a more ionic compound (Al_2S_3) leads to an increase in the latter of the covalent bond character, as a result of which the interatomic distance Al–S is reduced. The addition of Ga_2S_3 to ZnS, the ionic character of the bond of which is similar, scarcely changes the Ga–S distance. The lack of data on charge distribution in lanthanide sulphides precludes an analogous comparison, but the increase of the L–S distance suggests that the covalent bond character in L_2S_3 is smaller than in the MS compounds investigated.

Apart from the systems described, some results in the literature cannot be arranged systematically in a similar manner because of the lack of essential data[30,31].

The miscibility of sulphides increases greatly when one of the system components is a double sulphide. Thus the sulphides of bismuth and lead are almost immiscible, but 1.7 and 10 mole % PbS dissolves in $AgBiS_2$ at 200°C and 615°C respectively. Bismuth sulphide forms mixed crystals with $AgBiS_2$, in which the maximum Bi_2S_3 content is 16 mole %, and 14 mole % $AgBiS_2$ dissolves in PbS at 195°C.[26] It is believed that the increased miscibility of the components is due to the replacement of Ag^+ and Bi^{3+} by $2Pb^{2+}$ with formation of a cubic structure. The replacement in $AgBiS_2$ of silver by thallium, the dimensions of which are closer to those of lead and bismuth, leads to the formation of a continuous series of solid solutions in the system PbS–$TlBiS_2$.[32] The lower miscibility of PbS and $AgBiS_2$ is probably due not only to the greater difference between the dimensions of the metal atoms but also the inadequate homogenisation of mixtures of the systems. The regions of solid solutions in the systems $CuGaS_2$–ZnS and $AgGaS_2$–ZnS correspond respectively to 40 and 5–10 mole % ZnS.[33] The investigators concerned believe that the smaller solid solution region in the system with $AgGaS_2$ is not due to steric hindrance to the replacement of silver by zinc but is caused by the greater departure of the unit cell from the pseudocubic form. The spinels $MgIn_2S_4$, $CrIn_2S_4$, $MnIn_2S_4$, $CdIn_2S_4$, and $CoIn_2S_4$ form with In_2S_3, and $ZnAl_2S_4$ with Al_2S_3, an almost unlimited region of solid solutions[14,34]. An exception is $CaIn_2S_4$. It has been noted that in the region rich in MS solid solutions are not formed[14]. This phenomenon is probably due to the fact that the lattice constants of the spinel and the trivalent metal sulphide differ less than for the sulphide MS.

$PbSnS_2$ forms a two-sided solid solution with the initial components in which the region of homogenisation corresponds to about 30–53 mole % PbS.[35-37] The existence of a more extensive region of solid solutions of $PbSnS_2$ with SnS than with PbS can be accounted for by the similarity of their lattice constants.

According to X-ray diffraction data, the thiochromate spinel systems $ZnCr_2S_4$–$CdCr_2S_4$ and $FeCr_2S_4$–$CdCr_2S_4$ form a continuous series of solid solutions, due to the similarity of the atomic radii of zinc, cadmium, and iron[28].

Complete miscibility of the components is also observed in the systems Ag_3AsS_3–Ag_3SbS_3 and Ag_8GeS_6–Ag_8SnS_6.[38,39] It can be supposed that in the system Ag_8SnS_6–Ag_8SiS_6, whose compounds are isomorphous, unlimited miscibility should be observed.

The ready formation of solid solutions with complex sulphides and the unlimited miscibility of the components suggest that in the compounds described the metals are not divided into cations and anions but are distributed statistically in the tetrahedral and octahedral vacancies in the sulphur sublattice.

As mentioned above, solid solutions of simple sulphides are formed when the crystal structures, chemical bond type, and the effective radii of the metals undergoing mutual substitution are similar. As the composition of the compounds becomes more complicated, the above criteria lose their value. For double sulphides, the following factor evidently limits the miscibility: the dimensions of the vacancies in the sulphur sublattice do not exceed 0.76 Å,[13] while the effective radii of the majority

of metals are much greater and therefore the incorporation of the latter leads to the deformation of the lattices and the polarisation of sulphur. The formation of a double sulphide is favoured by a high temperature and the unsaturation of the chemical affinity of the sulphide sulphur. At the same time the constant of the sulphur sublattice increases, which creates favourable conditions for a freer substitution of the metals. This is also facilitated by the absence of acid radicals from many double sulphides of the type $[M_2S_4]^{2-}$, $[MS_6]^{8-}$, etc.

2. The Formation of Complex Sulphides

Systematic studies of sulphide systems at high temperatures were carried out by Flahaut, Hahn, and their coworkers. The most complete studies have been made on complex sulphides formed by mono-, tri, or di-valent metals with the general composition $M^IM^{III}S_2$, where M^I = Li, Na, K, Rb, Cs, Cu, or Ag and M^{III} = B, Al, Ga, In, P, V, As, Sb, Bi, Cr, Ti, Fe, or Ni.[3,18,26,40,41,64-66,70,72-75,79,97,114,183,199-206] Some investigators are inclined to attribute to the above compounds the formula $M^I_2M^{III}_2S_4$ in order to draw an analogy with the double sulphides $M^{II}M^{III}_2S_4$, where M^{II} = Cu, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Mn, Fe, Co, Ni, Pb, Yb, Sm, or Eu and M^{III} = B, Al, Ga, In, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Ti, Zr, As, Sb, Bi, Cr, Fe, Co, or Ni.[3,14,19,21,22,26,42,44,46-63].

The chemical stability of the sulphides described in relation to acids and alkalis is much greater than that of the individual compounds. Thus, whereas Al_2S_3, Ga_2S_3, and Cr_2S_3 are readily hydrolysed in moist air, $Li_2Ga_2S_4$, $Li_2In_2S_4$, $Rb_2Ga_2S_4$, $Cs_2Ga_2S_4$, $Rb_2In_2S_4$, and $Cs_2In_2S_4$ are not decomposed by water[64-66] and $Na_2Ga_2S_4$ and $K_2In_2S_4$ form hydrates. The double sulphides $MBiS_2$ (M = alkali metal) are stable in relation to water and $CuAlS_2$ is actually stable in relation to dilute hydrochloric acid at normal temperatures.

Many of the sulphides quoted above are not decomposed at high temperatures, which permits their purification by recrystallisation from a melt of halide salts with the same cation M,[48] or with the acid of gas-transport reactions[46,48]. The stability of the compounds formed by the interaction of the sulphides of zinc subgroup metals and gallium increases on going from double sulphides containing mercury to those with zinc and from the double sulphides with aluminium to those with indium, but it is lower than the stability of the analogous oxygen compounds.

Sokolov[67] proposed an empirical rule to determine whether the formation of compounds in binary sulphide systems is possible; it assumed that the reactions occur when the interatomic distance between the anion and the complex-forming cation in the crystalline state is smaller than the distance between another cation and the anion. However, in many systems mutual coordination of the initial compounds is observed as a function of their relative amounts (for example, $4Cu_2S.Na_2S$ and $Cu_2S.9Na_2S$). The above deficiencies make it difficult to extend the rule to many sulphide systems and therefore it will not be employed in the present review.

There exist three types of sulphide crystal lattices: chalcopyrite, spinel, and salt-like.

Double sulphides containing mono- and tri-valent metals crystallise with a chalcopyrite structure, the position of the atoms corresponding to a distorted tetragonal zinc blende structure with a statistical distribution of the metals. According to the data of Hahn et al.[19], many simple sulphides tend to undergo tetrahedral coordination, but this is prevented when the metal : sulphur ratio is greater or smaller than unity. This obstacle is eliminated in the interaction of two sulphides ($M_2S + M_2S_3$) which form compounds with a zinc blende structure and the corresponding electron distribution. This increase in the symmetry of double sulphide crystals is probably caused (as was observed in the formation of solid solutions) by the tendency of sulphur to form its own sublattice. In most cases the metals in the compounds differ in their radii, charges, and polarisation properties and therefore the formation of a wurtzite or zinc blende structure is different. The chalcogenides of mono- and tri-valent metals frequently have the chalcopyrite structure, in which there is an ordered arrangement of the metals in accordance with their properties.

The spinels include double sulphides, the composition of which is described by the formula $M^{II}M^{III}_2S_4$; they have the wurtzite or zinc blende structures. The high symmetry of the crystals is caused, on the one hand, by the tendency of sulphide sulphur to form its own lattice and, on the other hand, by the presence in most metals of a filled d level, as a result of which they tend to form with non-metals covalent bonds with sp^3 orbitals and a tetrahedral configuration[19]. Spinels are divided into normal and inverse depending on the distribution of the metal in the vacancies of the sulphide sulphur lattice. In the first type M^{II} atoms are distributed in tetrahedral vacancies and M^{III} atoms in octahedral vacancies, while in the second type M^{II} and M^{III} occupy simultaneously both octahedral and tetrahedral sites. This phenomenon is due to the relative ionic radii of the metals[51]. Depending on whether the radius of M^{II} is greater or smaller than that of M^{III}, the normal or inverse spinel is formed. However, this rule, as well as the rule designed to determine the lattice energy, the polarisation of sulphur, or the relative bond energies, is not always obeyed in practice. For example, at normal temperatures the "thiogallate structure"[19] resembles that of β-Cu_2HgI_4, but at higher temperatures it undergoes a transition to a zinc sulphide lattice with a statistical distribution of the metals.

Furthermore, indium, tin, and lanthanides form sulphides with the composition M_3S_4. X-Ray diffraction and magnetic studies of these compounds confirmed the existence in them of di- and tri-valent metals, so that the phase can be regarded as the spinel $M^{II}M^{III}_2S_4$.[52,68,69]

Taken together the above data lead to the conclusion that double sulphides with the composition $M^IM^{III}S_2$ or $M^{II}M^{III}_2S_4$ are formed only in those cases where the initial sulphides M^I_2S, $M^{II}S$, and $M^{III}_2S_3$ crystallise in a system of high symmetry and the polarisation properties of the metals are very weak.

The polarisation of sulphide sulphur by metals in the formation of double sulphides has attracted much attention[19,51]. Indeed the radii of covalent or ionic sulphur are much greater than those of oxygen and therefore, under the action of multicharged ions, sulphur should be considerably polarised. Compairson of the polarising capacities of zinc subgroup and Group III metals shows that, on going from zinc to mercury, there is a tendency for metals to be polarised, while on going from indium to boron there is a considerable increase in the polarisability of sulphur. Thus both in the transition from indium to boron and from zinc to mercury the electron density in double sulphide crystals will deviate to the maximum extent from that for wurtzite or zinc blende, which in turn will tend to loosen the structure and ultimately will in general lower the

stability of the double sulphide. This factor readily accounts for the stability and the possibility of the formation of double sulphides with the compositions discussed. Thus so far, it has proved impossible to obtain the spinels MAu_2S_4 (M = Mg, Zn, Cu^{II}, Ti^{II}, Sn^{II}, Pb, Mn^{II}, or Fe^{II}), and also the compounds $MgAl_2S_4$, $CuAl_2S_4$, $FeAl_2S_4$, $CoAl_2S_4$, and $NiAl_2S_4$, which have been described for indium. The sulphides of elements in the lowest state of oxidation (VS, SnS, TiS, Ti_2S_3, etc.) also fail to form spinels with trivalent metals [29,51,55,70].

Triple sulphides with the composition Cu_2ZnSnS_4, Cu_2CdSnS_4, and Cu_2HgSnS_4 have the zinc blende structure and the compound $CuZn_2GaS_4$, the existence of which has not been quite convicingly demonstrated as yet, crystallises in the hexagonal system [33,71]. It is interesting to note that the analogous compound Cu_2FeSnS_4 has been described as a mineral.

Crystallographic studies of the sulphide $CuPS_2$ showed that this compound crystallises with a würzite lattice and its structure is analogous to that of $CuBS_2$, where sulphur and boron or copper atoms are believed to alternate [203].

On the basis of the above data, one may conclude that the statistical distribution of metals in the vacancies of the sulphur lattice is more likely than the salt-like structure. Thus the data quoted do not justify the classification of the compounds described above as salt-like, which means that they cannot be approached from the standpoint of the acid–base theory. Therefore one can hardly agree with the statement [64] that potassium thioindate can be regarded as the salt of the dibasic acid $H_2In_2S_4$. The absence of salt-like properties in these compounds is confirmed by the following data. If CuV_2S_4 is regarded as a salt, then copper should be replaced by other metals. In fact the attempts to replace copper by zinc, cadmium, or mercury proved to be unsuccessful [3,72,73]. Rüdorff and Stegemann [74] established that the formation of $K_2Cr_2S_4$ is much more difficult than the formation of $Na_2Cr_2S_4$. On the basis of the chemical and crystallographic properties of potassium thiochromite, it was concluded that its lower stability is due to the different polarising properties of the alkaline metals, which is hardly ever observed for salt-like compounds. When the sulphide $Na_2Fe_2S_4$ is treated with a solution of a silver salt, the silver replaces not only the sodium but also part of the iron [75].

Only a few compounds have been classified as salt-like double sulphides with the composition $M^{II}M^{III}S_2$ or $M^{II}M^{III}_2S_4$. Bokii et al. [76] and Betekhtin [77] suggest that the sulphides of trivalent arsenic, antimony, and bismuth be regarded as salts containing complex ions of the type $[ES_3]^{3-}$. However, as stated above, crystallographic study of such bismuth compounds showed that they have a structure of the sodium chloride type with a statistical distribution of the metal atoms. $SrAs_2S_4$, which crystallises with a zinc blende structure, evidently belongs to sulphides of the same type [73]. Furthermore, the double sulphides $Ag_{24}Sb_2S_{15}$, Ag_9SbS_6, Ag_5SbS_4, Ag_3SbS_3, and $Ag_2Sb_{12}S_{19}$, which occur in nature as minerals, cannot be readily regarded as derivatives of the corresponding acids. The behaviour of $PbBi_2S_4$, which crystallises in the orthorhombic systems with layers of bismuth and sulphur having the composition BiS_2^-, is somewhat unusual [78]. Alkali metal thioarsenites and thioantimonites may be classified as salt-like compounds.

The elements of the arsenic subgroup are known to form compounds in which they are present in the anionic form. On this basis, one might expect that in the interaction with sulphides the metal components of which tend to form cations, thio-salts should be formed. However, arsenic, antimony, and bismuth do not form double sulphides having the composition $M^{II}M^{III}_2S_4$ with metals of the calcium subgroup, zinc, beryllium, the iron-group metals, etc [73]. It is striking that As_2S_3, Sb_2S_3, and Bi_2S_3 crystallise in a system of lower symmetry (orthorhombic and monoclinic) than the other trivalent metal sulphides mentioned above. At the same time the products of their interaction with Cu_2S and Ag_2S crystallise with a lattice of the chalcopyrite type. Similiar phenomena were observed also for other sulphides, which leads to the conclusion that an increase in the symmetry of the low-symmetry crystals is possible only when two metal atoms, of different valence, can replace zinc atoms in the zinc blende structure without appreciable distortion of the latter. X-Ray diffraction studies of sodium and potassium thiochromites [74,79] led to the conclusion that –Cr–S–Na–S–Cr– layers in hexagonal positions form a close-packed structure of the sodium chloride type. The formation in this structure of CrS_2^- units permits the classification of these compounds as salt-like. It is interesting to note that the group of double sulphides with the composition $MNaS_2$ (M = Nd, Sm, Eu, Gd, Tb, Dy, Ho, or Er) have been assigned to this type of thio-compound [60].

Table 3. Composition of double sulphides containing Group IV elements.

ES_3^{2-}		ES_4^{4-}	ES_6^{8-}	$E_2S_5^{2-}$
Li_2SiS_3	$CaSiS_3$	Li_4SiS_4 Cd_2GeS_4 $La_4[GeS_4]_3$	Cu_8SiS_6	$Na_2Ge_2S_5$
Cu_2SiS_3	Cu_2SnS_3	Cu_4SiS_4 Hg_2GeS_4 $Ce_4[GeS_4]_3$	Ag_8SiS_6	$CaSi_2S_5$
Na_2GeS_3	K_2TiS_3	Mg_2SiS_4 Mn_2SiS_4 $Pr_4[GeS_4]_3$	Ag_8GeS_6	
Cu_2GeS_3	$SrTiS_3$	Ca_2SiS_4 Mn_2GeS_4 $Nd_4[GeS_4]_3$	Ag_8SnS_6	
$PbGeS_3$	$BaTiS_3$	Ca_2GeS_4 Pb_2SiS_4 $Sm_4[GeS_4]_3$		
K_2SnS_3	$BaZrS_3$	Ca_2SnS_4 Pb_2GeS_4 $Gd_4[GeS_4]_3$		

The sulphide of tetravalent elements form a series of compounds [39,61,70,75,80–96], which can be regarded as the salts of the corresponding acids (Table 3).

Comparison of X-ray diffraction data show that only the thio-compounds of silver crystallise in the cubic system [39,44], which is characteristic of simple compounds. The structure of double sulphides belongs to a system of lower symmetry—orthohombic and even monoclinic—but for the majority of sulphides it has not been elucidated at all.

Sulphides containing elements of the titanium subgroup and copper(I) are dimorphous. The existence of the anions $[SiS_3]^{2-}$ or $[SiS_4]^{4-}$ has been proved only for Li_2SiS_3 and Ca_2SiS_4. [80]

The presence in certain double sulphides of anions, the formal correspondence between these compounds and the usual salt-like compounds, the great tendency of Group IV elements to form anions, the low symmetry of the crystals of many of the compounds, and the more ready hydrolysis of Li_4SiS_4 and Ca_2SiS_4 compared with Li_2SiS_3 and $CaSiS_3$ permit the classification of these compounds as salt-like. Their greater basicity than that of salts of the corresponding oxygen acids can be accounted for by the greater size of sulphide sulphur compared with oxygen. However, the data quoted above do not explain the coordination of four, and even less so six, atoms (ions) of sulphur by silicon, germanium, and tin, the increase in crystal symmetry on going from double sulphides containing copper to those with manganese, the occurrence of hexagonal packing of

sulphide sulphur in Mn_2SiS_4 and Mn_2GeS_4 with the metal atoms distributed among the tetrahedral and octahedral vacancies, the decrease of reactivity in the series $SiS_2 > GeS_2 > SnS_2$, the acid properties increasing in the same sense, and the relatively high miscibility of silver thiostannate and thiogermanate over the entire concentration range, although the dimensions of the ions $[GeS_6]^{8-}$ and $[SnS_6]^{8-}$ should differ considerably.

The above group of compounds is located at the boundary between complex sulphides, which are typical for mono- or di- and tri-valent elements, and the thio-salts of metals of Groups V–VII. The complex sulphides containing alkali and alkaline earth metals and Group IV metals should probably also be classified as thio-salts. This conclusion is confirmed by data for the interaction between titanium or zirconium sulphides, on the one hand, and elements of the calcium subgroup and magnesium, on the other. Since the acid properties of zirconium disulphide are not very pronounced, a metal with very marked basic properties is required for the formation of a double sulphide. Among the metals enumerated above, barium has the most basic properties and this is why only $BaZrS_3$ is formed. Evidently the reaction with alkali metals will proceed much more readily, and hafnium sulphide will behave similarly. Titanium disulphide has more marked acid properties and therefore it forms two compounds—$SrTiS_3$ and $BaTiS_3$. The stability of the above sulphides increases from double compounds containing zirconium to those containing titanium. The findings described above agree well with data [70,95] showing the absence of interaction of TiS_2 with ZnS, CdS, HgS, MnS, FeS, and NiS.

These results are in conflict with the statement [95] that compounds of the type ABS_3 have a structure consisting of ions packed into groups $(AS_3)_n$, in which the radii of the ions A and S should not differ too much. The species B is disregarded. However, this explanation is not entirely satisfactory, since it is impossible to understand the reason for the higher reactivity of the sulphides of calcium subgroup metals with TiS_2 than with ZrS_2 or TaS_2.

Group V elements in the normal state of oxidation yield two series of double sulphides, which may be regarded as derivatives of mono- and tri-basic acids (Table 4). The compounds BPS_4 and $AlPS_4$ are isomorphous, crystallising in the orthorhombic system with formation of infinite chains, as in the case of SiS_2, aluminium and phosphorus being linked to one another via sulphur and each being surrounded by sulphur atoms distributed tetrahedrally. Monosubstituted sodium, silver, and thallium thiophosphates are polymeric [97]. X-Ray diffraction study of sulvanite [86,98] Cu_3VS_4 and infrared spectroscopic study of ammonium thiovanadate in solutions [101] showed the existence of the tetrahedra $[VS_4]^{3-}$, which are distributed as in β-K_2SO_4. In view of the short Cu–V interatomic distance in the crystal lattice, it is believed [86] that there is a bond between copper and vanadium. The diamagnetism of Cu_3VS_4, its low electrical conductivity at elevated temperature, and the fact that even part of the vanadium cannot be replaced by chromium, manganese, iron, cobalt, and nickel suggest the formula $Cu_3^{+}V^{5+}S_4^{2-}$. The diamagnetism of the sulphide Tl_3NbS_4 leads to the assignment of the formal valencies to the elements in the compound: $Tl_3^{+}Nb^{5+}S_4^{2-}$. As a result of the considerable asymmetry in the distribution of cations about sulphur, these ions are strongly polarised. Estimation of the degree of polarisation by calculating the electrostatic field confirmed that this energy constitutes a considerable part of the total lattice energy, which is greater than for the zinc blende structure. It is interesting to note that the analogous arsenic compound Cu_3AsS_4 has a covalent As–S bond, in contrast to sulvanite [86].

When vanadium in sulvanite is replaced by niobium and tantalum, which have greater atomic dimensions, the stability of the thio-compounds increases and the colour weakens, which can be accounted for by less intense polarisation of the elements.

Table 4. Composition of double sulphides containing Group V elements [76,86,97–100].

	ES_4^{3-}		ES_3^{-}
Cu_3VS_4	K_3VS_4	Tl_3VS_4	$(NaPS_3)_x$
Cu_3NbS_4	K_3NbS_4	Tl_3NbS_4	$CuVS_3$
Cu_3TaS_4	K_3TaS_4	Tl_3TaS_4	$CuTaS_3$
Cu_3AsS_4	BPS_4	$AlPS_4$	$(AgPS_3)_x$
Cu_3SbS_4			$(TlPS_3)_x$

The compound $CuTaS_3$ crystallises in the orthorhombic system, in which tantalum is surrounded octahedrally by six sulphur atoms with six bonds and a Cu–Ta metallic bond is present [86]. Similar double sulphides with thallium and potassium have been less investigated. In view of the isomorphism of K_3VS_4 and K_3TaS_4, it is believed that these compounds are also salt-like, but some investigators deny the isomorphism of KVS_3 and K_3VS_4 [sic], since in this case the tetrahedra should be combined in a different way.

The data quoted show that the double sulphides described above, containing Group V elements in the highest state of oxidation, are similar to the oxygen-containing compounds and may be classified as thio-salts containing the ions $[ES_3]^{-}$ or $[ES_4]^{3-}$. The compounds exhibit different stabilities towards moisture, acids, and alkali. Thus, while sodium, boron, and aluminium thiophosphates readily undergo complete hydrolysis in moist air, K_3VS_4 hydrolyses only after dissolution; $(TlPS_3)_X$ and $(AgPS_3)_X$ are oxidised only with nitric acid on heating, and sulvanite Cu_3VS_4 occurs as a mineral. It has been noted that the compounds Tl_3ES_4 (E = V, Nb, or Ta) are sparingly soluble in water [86]. The melting points of these double sulphides are in the range 300–500°C. Studies on the electrical conductivity of the sulphides suggest that they are semiconductors.

The data for the interaction of the sulphides of lanthanides (L_2S_3) and aluminium or gallium with formation of compounds having the composition $AlL^{III}S_3$ (L^{III} = La, Ce, Pr, Nd, Sm, Gd, or Y), $GaL^{III}S_3$ (L^{III} = La or Y) [102,103], and $YInS_3$ [103–105] are insufficient for their assignment to any of the classes described above. Most of them crystallise in the hexagonal system ($YInS_3$ crystallises in the orthorhombic system). With certain component ratios, glasses are produced. The compounds are stable towards water, alkalis, weak mineral and organic acids, and organic solvents [104]. It is suggested that a covalent–ionic bond is present in the molecule of the sulphide $ML^{III}S_3$. [105] In accordance with the type of crystal lattice and composition, the sulphides $FePS_3$, $CoPS_3$, and $NiPS_3$ may be included among these compounds [106].

Apart from the classes of compounds described above, there is much information in the literature concerning the existence of compounds with more complex chemical compositions (Table 5). The ratios of the initial sulphides in these compounds range mainly from unity to five. However, in some cases fractional ratios occur, for example

in $5Na_2S.2Fes$, $5Cu_2S.2Na_2S$, $5PbS.4Sb_2S_3$, and $2L_2S_3.3GeS_2$, where L is a lanthanide [40,83,107-110], reaching nine in only a few cases, namely in $9Na_2S.Cu_2S$. [107,108]. Their crystal structures are also different, but the most characteristic feature of all of them is the absence of acid and basic groups.

Table 5. Composition of complex sulphides obtained by the thermal method.

Composition of compound	No. of valence electrons	Composition of compound	No. of valence electrons	Composition of compound	No. of valence electrons	Composition of compound	No. of valence electrons
$Cu_2S\cdot 3Ag_2S$	8	$SnS\cdot 4FeS$	10	$CaS\cdot 2Y_2S_3$	14	$DyS\cdot 2Dy_2S_3$	14
$Rb_2S\cdot 3Bi_2S_3$	20	$CuS\cdot 2FeS$	6	$MgS\cdot 2Y_2S_3$	14	$TuS\cdot 2Tu_2S_3$	14
$3Cu_2S\cdot As_2S_3$	12	$ZnS\cdot 2BaS$	6	$SrS\cdot 2Y_2S_3$	14	$HoS\cdot 2Ho_2S_3$	14
$3Cu_2S\cdot Sb_2S_3$	12	$SnS\cdot PbS$	4	$BaS\cdot 2Y_2S_3$	14	$SiS_2\cdot 2Li_2S$	8
$3Cu_2S\cdot Bi_2S_3$	12	$SiS_2\cdot 2MgS$	8	$FeS\cdot 2Y_2S_3$	14	$SiS_2\cdot 2Cu_2S$	8
$Ag_2S\cdot 3Bi_2S_3$	20	$SiS_2\cdot 2CaS$	8	$MnS\cdot 2Y_2S_3$	14	$SiS_2\cdot 4Ag_2S$	12
$Li_2S\cdot 5Al_2S_3$	32	$SiS_2\cdot 2MnS$	8	$CdS\cdot 2Y_2S_3$	14	$GeS_2\cdot 4Ag_2S$	12
$Cu_2S\cdot 5Al_2S_3$	32	$SiS_2\cdot 2PbS$	8	$CrS\cdot 2Y_2S_3$	14	$SnS_2\cdot 4Ag_2S$	12
$Ag_2S\cdot 5Al_2S_3$	32	$GeS_2\cdot 2CaS$	8	$MgS\cdot 2Dy_2S_3$	14	$2PbS\cdot B_2S_3$	10
$Ag_2S\cdot 5La_2S_3$	32	$GeS_2\cdot 2CdS$	8	$CdS\cdot 2Dy_2S_3$	14	$2PbS\cdot Al_2S_3$	10
$Ag_2S\cdot 5Ce_2S_3$	32	$GeS_2\cdot 2HgS$	8	$MnS\cdot 2Dy_2S_3$	14	$2GaS\cdot Ga_2S_3$	10
$Ag_2S\cdot 5Pr_2S_3$	32	$GeS_2\cdot 2MnS$	8	$CrS\cdot 2Ho_2S_3$	14	$2PbS\cdot Sb_2S_3$	10
$Ag_2S\cdot 5Nd_2S_3$	32	$GeS_2\cdot 2PbS$	8	$MgS\cdot 2Ho_2S_3$	14	$2PbS\cdot Bi_2S_3$	10
$Ag_2S\cdot 5Sm_2S_3$	32	$SnS_2\cdot 2CaS$	8	$CdS\cdot 2Ho_2S_3$	14	$2FeS\cdot 5Na_2S$	14
$Ag_2S\cdot 5Gd_2S_3$	32	$Cu_2S\cdot ZnS\cdot SnS_2$	8	$MnS\cdot 2Ho_2S_3$	14	$3GeS_2\cdot 2La_2S_3$	24
$Ag_2S\cdot 5Dy_2S_3$	32	$Cu_2S\cdot CdS\cdot SnS_2$	8	$FeS\cdot 2Ho_2S_3$	14	$3GeS_2\cdot 2Ce_2S_3$	24
$5Cu_2S\cdot Fe_2S_3$	16	$Cu_2S\cdot HgS\cdot SnS_2$	8	$CrS\cdot 2Ho_2S_3$	14	$3GeS_2\cdot 2Pr_2S_3$	24
$3Cu_2S\cdot 5Bi_2S_3$	36	$Cu_2S\cdot Al_2S_3\cdot 2SnS_2$	16	$MgS\cdot 2Er_2S_3$	14	$3GeS_2\cdot 2Nd_2S_3$	24
$3Cu_2S\cdot Tb_2S_3$	12	$Cu_2S\cdot In_2S_3\cdot 2SnS_2$	16	$CdS\cdot 2Er_2S_3$	14	$3GeS_2\cdot 2SmS_3$	24
$3Cu_2S\cdot Dy_2S_3$	12	$Cu_2S\cdot Cr_2S_3\cdot 2SnS_2$	16	$MnS\cdot 2Er_2S_3$	14	$3GeS_2\cdot 2Gd_2S_3$	24
$3Cu_2S\cdot Ho_2S_3$	12	$Cu_2S\cdot Cr_2S_3\cdot 2ZrS_2$	16	$FeS\cdot 2Er_2S_3$	14	$2GeS_2\cdot Na_2S$	10
$3Cu_2S\cdot Er_2S_3$	12	$Cu_2S\cdot Cr_2S_3\cdot 2TiS_2$	16	$CrS\cdot 2Er_2S_3$	14	$GeS_2\cdot 2Na_2S$	8
$3Cu_2S\cdot Tu_2S_3$	12	$Cu_2S\cdot Cr_2S_3\cdot 2HfS_2$	16	$MgS\cdot 2Tu_2S_3$	14	$3ZnS\cdot K_2S$	8
$3Cu_2S\cdot Yb_2S_3$	12	$Ag_2S\cdot In_2S_3\cdot 2SnS_2$	16	$CdS\cdot 2Tu_2S_3$	14	$3CdS\cdot K_2S$	8
$3Cu_2S\cdot Y_2S_3$	12	$Ag_2S\cdot Cr_2S_3\cdot 2SnS_2$	16	$MnS\cdot 2Tu_2S_3$	14	$3MnS\cdot K_2S$	8
$3Cu_2S\cdot Lu_2S_3$	12	$GeS_2\cdot 4CdS$	10	$FeS\cdot 2Tu_2S_3$	14	$3PbS\cdot Na_2S$	8
$Cu_2S\cdot Ag_2S$	4			$CrS\cdot 2Tu_2S_3$	14	$3InS\cdot In_2S_3$	12
$Al_2S_3\cdot La_2S_3$	12			$MgS\cdot 2Yb_2S_3$	14	$3ZnS\cdot In_2S_3$	12
$Al_2S_3\cdot Ce_2S_3$	12			$CdS\cdot 2Yb_2S_3$	14		
$Al_2S_3\cdot Pr_2S_3$	12			$MnS\cdot 2Yb_2S_3$	14		
$Al_2S_3\cdot Nd_2S_3$	12			$FeS\cdot 2Yb_2S_3$	14		
$Al_2S_3\cdot Sm_2S_3$	12			$CrS\cdot 2Yb_2S_3$	14		
$Al_2S_3\cdot Y_2S_3$	12						
$Ga_2S_3\cdot La_2S_3$	12						
$Ga_2S_3\cdot Y_2S_3$	12						
$In_2S_3\cdot La_2S_3$	12						
$In_2S_3\cdot Y_2S_3$	12						

Thus Flahaut et al. [111] and then Ballsstracci [112,113] obtained and investigated by X-ray diffraction compounds with the general formula $M_2S.5Al_2S_3$, when M = Li, Cu, or Ag, $Ag_2S.5L_2S_3$ (L = La, Ce, Pr, Nd, Sm, Gd, Tb, or Dy), and $3Cu_2S.L_2S_3$ (L = Tb, Dy, Ho, Er, Tm, Yb, Lu, or Y). They showed that aluminium-containing double sulphides crystallise with a spinel type of lattice, in which the monovalent metals and one fifth of aluminium are distributed in a random fashion among the tetrahedral vacancies. In the sulphide $Ag_2S.5L_2S_3$ the metal atoms are distributed statistically among the vacancies of the sulphide sulphur lattice.

Copper and iron sulphides interact with formation of the compounds Cu_5FeS_4 ($5Cu_2S.Fe_2S_3$), $CuFeS_2$ ($Cu_2S.Fe_2S_3$), and $CuFe_2S_3$ ($CuS.2FeS$), where the metal atoms in the crystal lattice occupy tetrahedral sites in a spinel type structure with a close-packed sulphide sulphur lattice [40,114].

The double sulphide Ba_2ZnS_3, [115] to which the incorrect composition $BaZnS_2$ was initially attributed [66] (this probably applies also to $SrZnS_2$), crystallises in the orthorhombic system. The Zn–S and Ba–S distances in this compound are almost equal to those in the initial sulphides, which also throws doubt on their salt-like structure. X-Ray diffraction confirmed the existence in the system PbS–Bi_2S_3 of double sulphides with the composition $Pb_2Bi_2S_5$ and $Pb_4Bi_2S_7$. [73,116] It has been established that the $Pb_2Bi_2S_5$ structure contains extensive regions of the zinc sulphide type [117].

Double sulphides with the composition MCu_4S_3 (M = K or Rb), which crystallise in the tetragonal system [118-120], have been described. The lattice consists of layers of –S–Cu–S–Cu–S– units, in which sulphur atoms form an almost regular tetrahedron. Copper is displaced from this tetrahedron into the layer formed by the alkali metal atoms. It is present in these compounds in the mono- and di-valent forms, but occupies identical positions regardless of valence, the layers constituting an integral whole and bearing a negative charge, i.e. $[Cu_4S_3]^-$.

Many of the sulphides listed in Table 5 have the sphalerite or zinc blende structure with a statistical distribution of metal atoms. This suggests that the compounds may be derived from the zinc sulphide structure, where the zinc sites are occupied by other metals and sulphide sulphur forms its own more or less distorted lattice. Goodman [121] and also Koshkin [122] believe that the chalcopyrite lattice of semiconductor compounds of the type $A^IB^{III}C_2^{VI}$, $A_2^IB^{IV}C_3^{VI}$, and $A^{II}B^{IV}C_3^{VI}$ resembles the sphalerite lattice, the difference being that the metal chalcopyrite sublattice contains atoms of two types. With a statistical distribution of metal atoms, the lattice of the three component compounds does not differ from that of sphalerite. The retention of the lattice properties in more complex sulphides suggests that the above hypotheses can be extended to the compounds under discussion.

However, the crystal-chemical properties of zinc sulphide requires that the following conditions be fulfilled. Since in the crystal lattice of the double sulphide the two metals must occupy at least two zinc positions, the number of valence electrons of the metal should be a multiple of four and the overall polarising capacity of the metals should be close to that of zinc in ZnS. Table 5 shows that all the compounds may be divided into two groups in accordance with the composition of the initial simple sulphides.

The first group includes the sulphides with metals having even or odd valences (for example $Cu_2S.Ag_2S$, $Li_2S.5Al_2S_3$, $GeS_2.2MS$, etc). The total number of valence electrons of the metals is a multiple of four. The data explain why in the sulphide systems where the metals have even or odd valences the initial components form only combinations in which the total number of valence electrons of the metals is a multiple of four and which have the composition $M_2S.M_2S_3$, $3M_2S.M_2S_3$, $M_2S.3M_2S_3$, and $M_2S.5M_2S_3$. The numbers of valence electrons in the molecules of the complex compounds are respectively 8, 12, 20, and 32, while the numbers corresponding to the compositions $2MS.M_2S_3$, $4M_2S.M_2S_3$, $M_2S.4M_2S_3$, and $M_2S.6M_2S_3$ are 10, 14, 14, 26, and 38 respectively. Therefore their existence is less likely.

A number of compounds with metals having different valences, where, as in the preceding case, the total number of valence electrons of the metals is a multiple of four, approach closely in their properties the sulphides of the above type. The thiospinels $M^{II}S.M_2^{III}S_3$, $3MS.K_2S$, and $3MS.In_2S_3$ should be included among them. As a rule, their crystals show high symmetry. Probably the combinations of these two factors is in fact decisive for the existence of compounds of this kind.

It is interesting to note that an increase in the complexity of the composition of sulphides of this type, for

example $Cu_2S.MS.SnS_2$ (M^{II} = Zn, Cd, or Hg), or $M^I_2S.M^{III}_2S_3.2M^{IV}S_2$ (M^I = Cu or Ag; M^{III} = Al, In, or Cr; M^{IV} = Ti, Zr, Hf, or Sn)[71,123] does not infringe the principle that the number of valence electrons of the metals must be multiple of four.

The second group includes complex sulphides consisting of elements with even and odd valences, the sum of the valence electrons of the metals of the coordinated sulphides being a multiple of four, for example $MS.2M_2S_3$, $2MS.M_2S_3$, etc., despite the different coordinating capacities of sulphides of this class.

Comparison of the available literature data shows that the coordination number of the simple sulphides combined in the complex depends on the position of the metals in the Periodic System; it increases with the atomic number of the complex-forming metal. As an example, one may quote the double sulphides which include Group I elements: $Na_2Mn_2S_4 \rightarrow K_2Mn_3S_4$; $Na_2Cu_3S_3 \rightarrow K(Rb)Cu_4S_3$; $M_2S.Bi_2S_3$ (M = Li, Na, or K) $\rightarrow Rb_2.3Bi_2S_3$; $Na_2S.Cr_2S_3 \rightarrow K_2S.2Cr_2S_3$; $Cu_2S.Bi_2S_3 \rightarrow Ag_2S.3Bi_2S_3$; etc. It has been noted that rubidium and bismuth sulphides do not form $Rb_2S.Bi_2S_3$. Thus, as the atomic number of the coordinating metal increases, the composition of stable double sulphides becomes more complicated.

III. INTERACTION OF SULPHIDES IN PRECIPITATION FROM AQUEOUS SOLUTIONS

As in fusion, the interaction of sulphides in their precipitation from solution reduces to the formation of solid solutions or double compounds, but the process itself takes place in a more complicated manner. This is because, apart from the conditions for the formation of solid solutions or complex sulphides described in the preceding sections, other factors influencing the process are the solubility of the sulphides (which varies within a wide range), the state of the metal in the initial solution, the stability of its complexes, and the presence of other substances which affect the formation of colloidal and crystalline particles.

For example the particular modification of cadmium sulphide obtained when it is precipitated from solutions depends both on the temperature and the composition of the initial salt[124].

One must agree with Feigl's view[7] that the above phenomena cannot be described solely in terms of the law of mass action or the solubility products. One of the main factors which influence the interaction of sulphides is the concentration in the solution of hydrogen sulphide and sulphide ions. This effect determines conditions for the formation of the precipitate and the acquisition of a charge by the latter. When the amount of hydrogen sulphide is insufficient, metal atoms are adsorbed on the surface of the precipitate by virtue of their high affinity for sulphur, and create a positive charge, while in the presence of an excess of hydrogen sulphide a negative charge is produced. In their discussion of the effect of hydrogen sulphide on coprecipitation, Kolthoff and coworkers[125,126] concluded that hydrogen sulphide and its ions favour the interaction of sulphides because their concentration is higher on the surface of the precipitate than in solution, which has been confirmed by the studies of Rudnev and Malofeeva[127-131]. The removal of hydrogen sulphide from the surface of the solid reduces or altogether suppresses the reactivity of the sulphides precipitated. The capacity for coprecipitation is partially or completely restored after repeated addition to the washed precipitate of water containing hydrogen sulphide. Therefore it is believed that the presence of hydrogen sulphide or its ions on the surface of the sulphide is an essential but not a decisive factor in coprecipitation. This hypothesis is confirmed by the studies of Vachnadze[132], which show that the existence of the compounds In_2S_3 and $MInS_2$ is determined by the relative amounts of In and M^I and not of the sulphide sulphur and indium, and also by the ion exchange between the sulphide precipitate and solution in the absence of adsorbed hydrogen sulphide. In the latter case the experiments were performed on columns containing freshly prepared sulphides of zinc, cadmium, and lead with solutions of copper, lead, manganese, cobalt, nickel, zinc, cadmium, and thallium(I) salts or the sulphides of iron, zinc, lead, cadmium, copper, and silver with solutions of mercury(II), copper(II), and silver salts[133-135]. It was shown that in all the experiments only copper was fully precipitated, while other ions either did not undergo quantitative exchange or their exchange was not consistent with the solubility products. It was noted that the exchange is retarded as the concentration of the precipitating metal in solution is reduced regardless of the solubility products of the sulphides, probably because diffusion of the metal ions through the layer of the corresponding sulphides is difficult. It is interesting to note that the rate of exchange with the less soluble cadmium sulphide is much higher than with the more soluble zinc sulphide, while complete exchange between As_2S_3 and silver ions is not achieved in practice. It is believed that in this case the double sulphide Ag_3AsS_3 is formed and is not decomposed by the excess silver ions. Mercury is precipitated in the form of the compounds xHgS.yHgHal$_2$. There is no ion exchange between zinc sulphide and arsenic, germanium, and indium salts, but the degree of precipitation of indium from solutions containing all the above metals increases under analogous conditions, while that of germanium falls[136], which we believe to be related to the formation of solid solutions of indium and arsenic sulphides or double sulphides. The investigators concerned have correctly noted that the absence of a rigorous relation between the results and the solubility products of the sulphides can be explained by the low reliability of the solubility products and the lack of data for their variation with the size of the precipitated crystals and the particular modification of the sulphide. Indeed, according to data in handbooks[137], the solubilities quoted for the same sulphide differ by 2–6 powers of ten. The results show that the suggestions by Ruff and Hirsch[138] to use as the criterion of the possibility of separation the ratio $SP_1 : SP_2 = K$, where SP_1 and SP_2 are the solubility products of the sulphides to be separated, is erroneous. For high values of K, the sulphides should be separated quantitatively and equilibrium should be attained rapidly. It has now been established that NiS ($SP = 10^{-21}$–10^{-28}) coprecipitates most readily with SnS_2, Bi_2S_3, and FeS, whose solubility products are smaller, and K for Bi_2S_3 is 10^{44}, while MnS ($SP = 10^{-15}$) is most readily coprecipitated with SnS_2 and HgS, where $K = 10^{28}$, the extent of coprecipitation with sulphides whose solubility products are much higher being appreciably less. Nor can one agree with the view put forward by Troitskii[139], who accounts for deviations of this kind by adsorption or by the presence in the precipitate of impurities more soluble than the element coprecipitated.

Many investigators noted long ago that the sorption capacity of the sulphides precipitated from solutions is different in the presence of organic compounds, where were therefore used to suppress coprecipitation[140-142]. The reason for this phenomenon is the interaction of the

oppositely charged colloidal particles of the organic substance and the sulphide sol with possible formation of chemical compounds [143,144]. Sulphides react most fully with triphenylmethane dyes and certain azine dyes, whereby it is possible to prevent completely the coprecipitation of metals with sulphides. This is also favoured by the formation of stable complexes of the coprecipitating metal with the organic compound.

The study of the sorption capacity of a group of sulphides, using as an example the dye Neutral Red, showed that the sorption capacity of bismuth, antimony, mercury, and tin sulphides increases with time, that of arsenic and lead sulphides decreases, and that of copper, silver, and cadmium sulphides remains unchanged [143,145]. The authors believe that this is due to a change in the state of aggregation of the sulphides. However, the results of studies on the coprecipitation of gallium subgroup metals with copper, cadmium, mercury(II), and thallium(I) sulphides and with Bi_2S_3 showed [146,147] that the attempts to extend these findings to the coprecipitation of metals were unsuccessful. Similar results were obtained in the study of the effect of the surface area of the sulphides formed and their charge on their reactivity [145,148,149].

It may be supposed that the degree of coprecipitation should be a minimum in the presence of organic substances and when organic sulphur-containing substances, which do not produce sulphide ions in the solution, are employed. Ion exchange can be successfully used to concentrate elements forming sparingly soluble sulphides.

The interaction of metal salts and hydrogen sulphide may take place via the formation of normal (MS), acid $[M(HS)_2]$ and mixed ($M^{I}SM^{II}$) compounds [150,151]. Furthermore, it is also complicated by the presence in the inner sphere of the complex cation of coordinated water and hydrogen sulphide, which are capable of forming stable hydrogen bonds [152-155].

Thus the data obtained by investigators attempting to find the physical causes of coprecipitation [138,139,156-160] yielded convincing proof of one of the first hypotheses put forward by Feigl [7,161], namely that the reason for the interaction between sulphides is the coordination unsaturation of sulphide sulphur, as a result of which the formation of solid solutions and double sulphides is possible. Physical factors merely increase or decrease the degree of coprecipitation but are not decisive for the reactivity of sulphides. Their interaction with formation of double compounds must be determined by the thermodynamic quantities which include in the first place the affinity of the metals for sulphur, the latter decreasing with enhancement of the non-metallic properties of the elements in the series Zn > Mn > (Co) > Cd > Cu > (Ni) > Fe > Rb > Sn > Ag > Sb > Bi. [162] Furthermore, as pointed out by Yatsimirskii [163], stable thio-salts are formed in those cases where the sulphides have pronounced electrostatic and covalent characteristics.

All the findings described above suggest that the most reliable results can be obtained only by employing the method of physicochemical analysis in combination with crystallographic hypotheses concerning the structure of the above class of compounds. The application of physicochemical analysis to coprecipitation processes, which was first justified by Rudnev and Malofeeva, permitted a deeper understanding of this phenomenon. However, we believe that, when phase diagrams are plotted, a somewhat arbitrary procedure is employed. Usually coprecipitation is studied under conditions excluding the deposition of an independent phase consisting of one of the sulphides. Therefore in the formation of complex compounds the ratio of the amounts of the metals in the precipitate is smaller than in the solution. As the equivalence point is approached, the degree of coprecipitation diminishes due to the decomposition by the medium of the double sulphide formed and the difficulty of attaining the true state of equilibrium because of the rapid precipitation of the solid phase. Therefore the coprecipitation curve obtained by plotting $M:M_1$ (solution) against the degree of precipitation of M(%) will describe the interaction processes only when a single stable complex sulphide is formed (Table 6). When several compounds exist in the system, the curves will reflect only the most stable compound, which is not the case when the results are represented by plots of $M:M_1$ (precipitate) against $M:M_1$ (solution). Therefore in order to avoid an incorrect interpretation of the results, experimental data should always be represented by plots of the latter type.

Table 6. Comparison of the results of interaction studies of sulphides on the basis of different plots.

System	Interaction of sulphides based on different plots		Refs
	$M:M_1$ (soln.)–degree of precipitation, %	$M:M_1$ (soln.)–$M:M_1$ (ppt.)	
Tl_2S — Re_2S_7	$TlReS_4$	$2Tl_2S\cdot Re_2S_7$—$3Tl_2S\cdot Re_2S_7$	127, 165
In_2S_3 — Re_2S_7	solid soln	$In_2S_3\cdot Re_2S_7$	180
Tl_2S — PtS_2	$TlPtS_3$	$Tl_2S\cdot 2PtS_2$	130
Tl_2S — In_2S_3	$TlIn_2S_3$	$Tl_2S\cdot 2In_2S_3$	167
Tl_2S — GeS_2	$TlGeS_3$	$3Tl_2S\cdot 2GeS_2$	164
Tl_2S — Ru_2S_3	$TlRu_2S_2$	$Tl_2S\cdot 2Ru_2S_3$	129
In_2S_3 — SnS_2	solid soln.	solid soln.	168, 169
Tl_2S — Bi_2S_3	$TlBiS_2$ or solid soln	$Tl_2S\cdot 2Bi_2S_3$	171
CdS — HgS	solid soln.	CdS·HgS	172, 173
In_2S_3 — GeS_2	$InGe_3S_5$	$3In_2S_3\cdot 2GeS_2$ and $In_2S_3\cdot 6GeS_2$—$In_2S_3\cdot 2GeS_2$	164
Tl_2S — Sb_2S_3	$Tl_3Sb_2S_2$	$2Tl_2S\cdot Sb_2S_3$ or Tl_3SbS_3	164
Tl_2S — PdS	$TlPd_2S_3$	$Tl_2S\cdot 4PdS$	164

The conclusions based on the results of the study of systems by the method of continuous variations alone are not sufficiently convincing, since this procedure involves the continuous variation of the amount of solid phase, which affects the degree of precipitation. This can probably account for the discrepancy between the results obtained in the study of the system Tl_2S–PbS by a thermal method, which indicates very limited miscibility [32], and by precipitation of the sulphides, which indicates unlimited miscibility of the solid solutions [164].

In connection with the formation in the system of several complex compounds or solid solutions and compounds, the method of preparation of double sulphides in the presence of a large excess of the coprecipitating metal is valid only if the formation of a single double sulphide has been proved. If the interaction takes place in a complex manner, the preparation of a stoichiometric sulphide requires the use of an acceptable excess, a more suitable acidity of the solution, or fusion.

1. Formation of Solid Solutions

A general defect of the studies relevant to this section is the lack of a rigorous proof of the individuality of the solid phases formed, as was the case in the fusion of the sulphides. Therefore sometimes, when the precipitation of solid solutions during coprecipitation is postulated, a clear distinction is not established between this process and the formation of double sulphides.

The possibility of the formation of a solid solution in the study of coprecipitation in the sulphide systems of zinc and manganese, cadmium and manganese, cadmium and mercury, manganese and mercury, and cobalt and tin was pointed out at an early stage by Feigl[7,161], who called such products "*misch*-sulphides", but this was disputed by Ruff and Hirsch.

The study of the interaction of the sulphides of indium and tin(IV), arsenic(III), bismuth, and cadmium[168,174] indicates the formation of solid solutions, the range of existence of which are various. The results have been explained by the similarity of the atomic radii and the crystallographic parameters, assuming the bonds in the sulphides to be covalent. However the conclusion[174] that "... with increase in the difference between the atomic radii of the metals replacing one another, the miscibility of the components in molecular solid solutions steadily diminishes" is controversial, since in reality similar degrees of coprecipitation have been obtained for pairs of metals differing appreciably in their radii.

The study of the interaction under similar conditions of the sulphides of gallium and tin(IV), copper(II), zinc, and cadmium[175-178] showed that the range of existence of the solid solutions depends on the similarity of the ionic radii of the metals and the ionic character of the metal–sulphur bond. Furthermore, it was established that the degree of precipitation of gallium is determined also by the concentrations of the metals in the initial solution when their relative amounts are kept constant. This is due to the concentration gradient of the coprecipitating element near the surface of the precipitate, caused by its rapid deposition. The subsequent equalisation does not have an appreciable influence on the process, since it is now determined by the diffusion coefficient of the coprecipitating metal in the solid phase. As an example, one may quote on the dissolution of indium coprecipitating with tin disulphide in hydrochloric acid of various concentrations, where it was established that, as the precipitate dissolves, the indium to tin ratio increases from 0.4 for the first portion to 0.8 when the precipitate has completely disappeared. The results suggest that, when solid solutions are formed, coprecipitation will be most complete in dilute solutions, since under these conditions a high degree of dispersion of the sulphide precipitate is maintained for a longer period. This creates favourable conditions for the system to approach a state of equilibrium. Indeed the degree of precipitation of gallium with zinc and copper sulphides increases as the concentration of the elements in the initial solution is reduced. Thus the above property of sulphide systems may serve as one of the criteria for the determination of the cause underlying the interaction of sulphides during their isolation from solution.

The results of the study of the interaction in the systems Tl_2S–As_2S_3 and Tl_2S–As_2S_5, where the existence of a limited region of solid solutions in the first system (100–62 mole % As_2S_3) and its absence in the second was demonstrated, confirm the conclusion of a significant role of metal ion dimensions in the process under discussion. The data concerning the unlimited miscibility in the systems Tl_2S–Sb_2S_3, Tl_2S–Sb_2S_5, and Tl_2S–SnS require revision, since the dimensions of the metal species differ appreciably from one another[179].

The lack of information about the ionic character of the bond for most of the sulphides described hinders the use of effective radii in the discussion of experimental data.

Thus in the formation of solid solutions of sulphides precipitated from solution the conditions established in the systems are not as severe as in fusion and therefore the degree of mutual replacement of the metals is less complete. This can probably explain the finding that in the region of solid solutions, even when the atomic or ionic radii and crystal chemical parameters are similar, the ratio of the metals in the precipitate does not exceed 1 : 0.1 (10%)[180,181].

The data on the effects of temperature on the interaction between sulphides in the formation of solid solutions are contradictory. Some workers believe that an increase of temperature reduces the degree of coprecipitation in the case of crystalline precipitates but has not effect if the sulphide is amorphous, while others think that it has no effect at all or increases the degree of coprecipitation[178,182,212].

The degree of coprecipitation of the metal depends to a considerable degree on the concentration of acid in the initial solution. This is because a decrease of acidity favours the precipitation of the second sulphide in consequence of secondary processes. In such cases the reason for the coprecipitation of the metal may be inferred only from X-ray diffraction data. Therefore sulphide systems must be studied under conditions such that the degree of coprecipitation is less than 100%. Then the formation of an independent or so called "colloidal" phase of the coprecipitating sulphide becomes impossible. The formation of the "colloidal" phase complicates the comparison of the conditions for the formation of solid solutions and double sulphides and the determination of the relations governing such processes. Evidently this can account for the discrepancy between the views of various workers on the effect of temperature and acidity of the medium on coprecipitation. The determination of the type of interaction of the sulphides from the chemical analysis of the solid phase precipitated is also doubtful[168].

Comparison of the data concerning the impurity content in minerals consisting of simple sulphides[183] confirms our earlier conclusion that the amount of impurities in compounds with a cubic lattice is much greater than for the same substances with a hexagonal lattice. Thus up to 26% of iron, 5% CdS, and 5.36% HgS have been found in cubic zinc sulphide, while in hexagonal zinc sulphide [the CdS content is (? Translator)] up to 8% and HgS was not detected. Manganese and zinc sulphides, which have similar effective radii and crystallise in the cubic system, contain a large number of metals at high concentrations. The impurities most frequently encountered are iron, copper, zinc, and manganese, which is probably due to the intermediate position of these metals in the series of effective radii.

An increase [decrease ? (Ed. of Translation)] in the content of isomorphous impurities in the series $Bi_2S_3 > Sb_2S_3 > As_2S_3$ takes place in parallel with the variation of the reactivity of the sulphides. This suggests that in this case complex sulphides and not solid solutions are formed.

The isomorphous substitution of elements in double sulphides can be followed most fully for compounds of the type $M_xE_yS_z$, where M^I = Cu or Ag, E^{III} = As, Sb, or Bi, $x = 1$ or 3, $y = 1$ or 3, and $z = 2$, 3, or 5. As the ratio M : E increases, there is an increase in the symmetry of the crystals of the complex sulphides, the impurity content, and the degree of mutual substitution of the E elements, but the degree of isomorphous substitution of the M elements diminishes.

Thus comparison of the relations obtaining in the formation of solid solutions formed by the fusion of sulphides or their precipitation from aqueous solution shows that in all cases the interaction in the systems is more complete when the radii of the metals corrected for the ionic charac-

ter of the M–S bond are similar and the crystal symmetry is high.

2. Formation of Complex Sulphides

There is less information about the interaction of sulphides during their precipitation from solutions (Table 7) than in the case of their heat treatment.

Hexavalent molybdenum and tungsten form thio-salts of the type $M^{I}_{2}ES_4$ derived from the corresponding acids H_2ES_4.[195,207-211] Infrared spectroscopic studies of the double sulphides in solutions and in the crystalline state showed that the existence of a tetrahedral configuration of sulphur atoms around the metal $[ES_4]^{n-1}$ is characteristic of elements in Groups V and VI, for which the existence of E=S double bonds has been demonstrated. The characteristic frequency of the E–S stretching vibrations is in the range 400–500 cm^{-1} [101,166,194]. Other elements, including rhenium(VII), do not form ions of this type, and therefore investigators [195,196] rejected the possibility of the formation of the thio-salts $KReS_4$ and $TlReS_4$. The absence of the E=S double bonds [194,197] in $[AsS_4]^{3-}$ and $[SbS_4]^{3-}$ also throws doubt on the salt-like nature of these compounds.

Table 7. Composition of double sulphides obtained by co-precipitation from solution [127,129,130,164,165,167-171,173,176-179,184-193,213].

Composition of compound	Sum of valence electrons	Composition of compound	Sum of valence electrons	Composition of compound	Sum of valence electrons	Composition of compound	Sum of valence electrons
$Ag_2S \cdot Au_2S$	4	$4CdS \cdot GeS_2$	12	$4ZnS \cdot In_2S_3$	14	$3ZnS \cdot Ga_2S_3$	12
$3Ag_2S \cdot Au_2S$	8	$4PbS \cdot GeS_2$	12	$4CuS \cdot Tl_2S$	10	$3CuS \cdot Ga_2S_3$	12
$Na_2S \cdot Fe_2S_3$	8	$2HgS \cdot SnS_2$	8	$4PdS \cdot Tl_2S$	10	$3SnS_2 \cdot Ga_2S_3$	18
$K_2S \cdot Fe_2S_3$	8	$CuS \cdot GeS_2$	6	$4Li_2S \cdot GeS_2$	12	$CaS \cdot Fe_2S_3$	8
$(NH_4)_2S \cdot Fe_2S_3$	8	$BaS \cdot CS_2$	6	$4Na_2S \cdot GeS_2$	12	$BaS \cdot Fe_2S_3$	8
$Tl_2S \cdot As_2S_3$	8			$4K_2S \cdot GeS_2$	12	$ZnS \cdot Ga_2S_3$	8
$Cu_2S \cdot In_2S_3$	8			$4Rb_2S \cdot GeS_2$	12	$CuS \cdot Ga_2S_3$	8
$Ag_2S \cdot In_2S_3$	8			$4Cs_2S \cdot GeS_2$	12	$CdS \cdot Ga_2S_3$	8
$Tl_2S \cdot In_2S_3$	8			$4Ag_2S \cdot GeS_2$	12		
$Bi_2S_3 \cdot Ga_2S_3$	24			$2CuS \cdot Tl_2S$	6		
$3Na_2S \cdot P_2S_5$	16			$2Tl_2S \cdot SnS_2$	10		
$K_2S \cdot Re_2S_7$	16						
$Tl_2S \cdot Re_2S_7$	16						
$Tl_2S \cdot Tl_2S_3$	8						
$H_2S \cdot B_2S_3$	8						
$3Tl_2S \cdot As_2S_5$	16						
$2Bi_2S_3 \cdot 3Ga_2S_3$	30						
$2Bi_2S_3 \cdot Ga_2S_3$	18						

Apart from the double sulphides quoted in Table 7, a number of others, where the metals are in an unusual valence state, have been described in the literature. These include $TlSnS_2$, $TlMoS_2$, $TlIn_2S_3$, $TlGeS_2$, $Tl_3Sb_2S_2$, Tl_3Ir_3S, $TlRh_2S_4$, $TlRu_2S_6$, $TlPd_2S_3$, $TlPtS_3$, $InGe_3S_5$, and ZnS.GaS.[166,198] According to data derived by physico-chemical analysis, the inflections in the coprecipitation curves reflect only the ratio of the metals in the compound formed. The sulphur content is determined by chemical analysis preceded by washing and drying of the precipitate, which can lead to a change in its composition. Indeed formulae for certain sulphides can be written assuming the metal to be present in different valence states, for example, $TlSnS_2$–$Tl_2S.SnS.SnS_2$, $TlIn_2S_3$–$Tl_2S.2InS.In_2S_3$, $InGe_3S_5$–$InS.2GeS.GeS_2$, etc. All the simple sulphides quoted here are obtained as a rule at elevated temperatures.

A general feature of the compounds listed in Table 7 is the fact that the sum of the valence electrons of the metal is a multiple of four (for the majority of the sulphides). As for the double sulphides obtained by the thermal method, these can be divided into two similar groups: metals with even or odd and mixed valences having analogous properties. It is interesting to note that some of the compounds listed have also been obtained by the thermal method, for example $Cu_2S.In_2S_3$, $Ag_2S.In_2S_3$, $Tl_2S.In_2S_3$, $ZnS.Ga_2S_3$, etc.

The results quoted show that, in their interaction, simple sulphides tend to form definite compounds regardless of the method used. The acid–base properties of the simple sulphides are not of decisive importance for their reactivity.

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Institute of General and Inorganic Chemistry,
Academy of Sciences of the Ukrainian SSR,
Kiev

U.D.C. 547.721

Methods of Synthesis of β-Substituted Furan Derivatives

L.D.Krasnoslobodskaya and Ya.L.Gol'dfarb

The review describes the methods of synthesis of β-substituted furan derivatives. Particular attention was devoted to the methods based both on furan itself and its α-monosubstituted derivatives. This approach to the problem arises from the fact that at the present time compounds of the furan series, for example furfural, furan, silvan, etc. are readily available and are manufactured on a commercial scale. The bibliography includes 202 references.

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I. INTRODUCTION

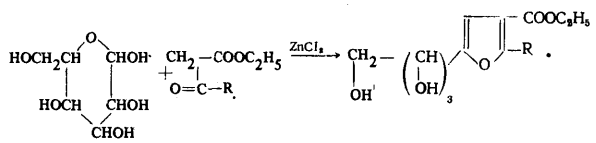
The most important distinctive feature of the furan system consists in its vigorously defined mode of interaction with electrophilic and nucleophilic agents: in all cases, when at least one α-position in the ring is free and the second α-position is not substituted by a very active group, for example a keto-group, the new substituent enters the α-position whatever its nature [1]. This gave rise to a definite trend in the development of the chemistry of furan. As a result α-mono- and αα'-di-substituted furan derivatives constitute so far the main bulk of the synthesised and investigated compounds of the furan series. At the same time many β-substituted derivatives have been obtained by an "indirect" method involving, in particular, the ring closure of the corresponding open-chain derivatives, which are frequently not readily available. However, it is evident that the interest in β-substituted furan derivatives will increase, since they are often encountered in natural products and sometimes exhibit physiological and other activity different from that of the isomeric compounds with substituents in the α-positions. As an example, one may quote the importance of the position of the nitro-group as a factor responsible for antibacterial activity [2].

II. METHODS OF SYNTHESIS OF TRI- AND TETRA-SUBSTITUTED FURAN DERIVATIVES

Since tri- and tetra-substituted furan derivatives (mainly tri-substituted) are the starting materials in the synthesis of β-mono-, 2,3-di-, and 2,4-di-substituted furan derivatives, it is desirable to describe in the first place the general methods for the preparation of these compounds.

1. Syntheses Based on Aliphatic β-Dicarbonyl Compounds

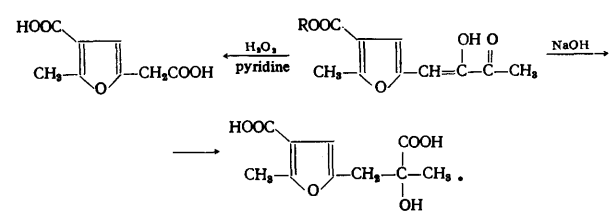
α-Substituted esters of furan-3-carboxylic acid (II) have been obtained by the reaction of acetoacetic ester, benzoylacetic ester, or the ester of acetonedicarboxylic acid with aldoses (I):[3,4]



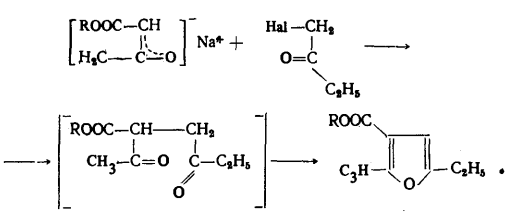
(I) (II)

Compound (II, R = CH_3) has been oxidised with potassium permanganate to 5-methylfuran-2,4-dicarboxylic acid and with periodic acid to the ester of 2-formyl-5-methylfuran-carboxylic acid.

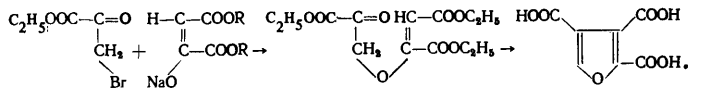
Recently Dalton [5] showed that, when compound (II) is heated in an ethanolic solution of hydrogen chloride, an α-diketone is formed. Under the action of hydrogen peroxide, the diketone is converted into 2-carboxymethyl-5-methylfuran-4-carboxylic acid, while in the presence of alkali it undergoes a benzilic acid rearrangement:



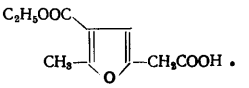
Tri-substituted furan derivatives are also obtained in the interaction of sodioacetoacetic ester and similar compounds with α-halogeno-ketones:[6-8]



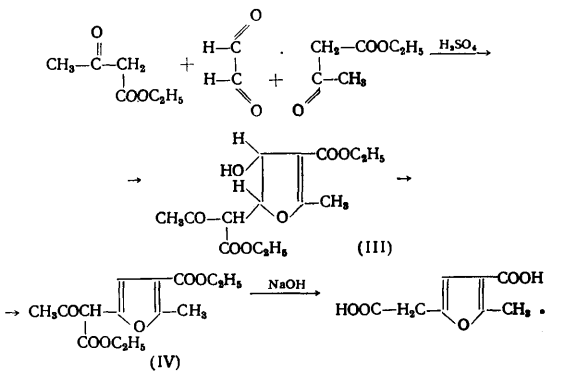
At the same time there are reactions regarded as examples of the interaction of an α-halogenocarbonyl compound with the sodio-derivative of a β-dicarbonyl compound via the oxygen atom. For example, Reichstein[9] described the reaction of the sodio-derivative of the oxaloacetic ester with monobromopyruvic acid, which was converted into furan-2,3,4-tricarboxylic acid:



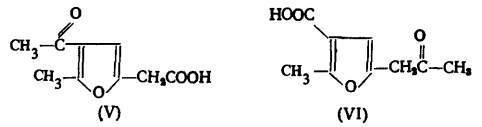
If the process proceeded via a 1,4-dicarbonyl compound, as suggested by Sutter[10], the reaction product would have been furan-2,3,5-tricarboxylic acid. When the acetoacetic ester is heated with the disodium salt of succinic acid in acetic anhydride, the monoethyl ester of 4-carboxy-5-methylfuran-2-acetic acid is formed:



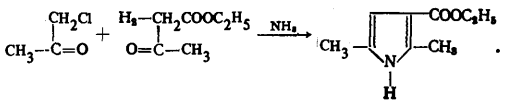
This synthesis was achieved for the first time by Fittig[11] and then by Reichstein and Grüssner[12]. Patent data published in 1959 show[13] that 4-carboxy-5-methylfuran-2-acetic acid can also be obtained by the condensation of acetoacetic ester with glyoxal in an acid medium:



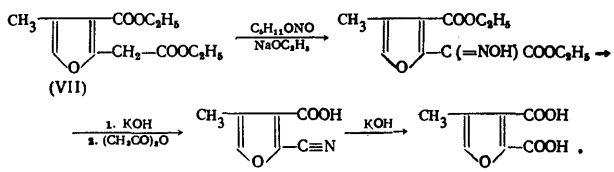
It has been shown that the process takes place via stages involving the formation of compounds (III) and (IV). The Fittig reaction was repeated in 1963 with acetylacetone by Suverkropp and Wynberg[14], who obtained 4-acetyl-5-methylfuran-2-acetic acid (V), which was then converted by decarboxylation into 3-acetyl-2,5-dimethylfuran. It proved to be identical with the product formed in the acylation of 2,5-dimethylfuran[15]. It is noteworthy that the structure of the isomeric 5-acetonyl-2-methylfuran-3-carboxylic acid (VI) was previously incorrectly attributed to compound (V):[16]



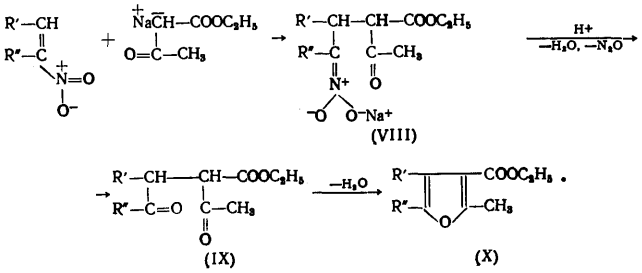
The syntheses of Feist[17] and Benary[18] are very close to the reactions of the sodio-derivatives of β-dicarbonyl compounds with α-halogeno-ketones. They consist in the interaction of β-dicarbonyl compounds with α-halogeno-ketones[17] or with α-chloroacetaldehyde[18] in ammonia. These reactions usually result in a mixture of pyrrole and furan derivatives, the relative amounts of which depend on the nature of the β-dicarbonyl compound employed. Thus, when acetoacetic ester is used, pyrrole derivatives are mainly obtained (the Hantzsch reaction):



With acetonedicarboxylic acid, the formation of the furan derivative (VII) predominates[17,19]. Starting with compound (VII), Rinkes[20] and Reichstein[19] achieved almost simultaneously the synthesis of 4-methylfuran-2,3-dicarboxylic acid, which can be illustrated by the following scheme:



Boberg and Schultze[21] synthesised a number of tri- and tetra-substituted furan derivatives by the reaction of sodioacetoacetic ester with α-nitro-olefins:

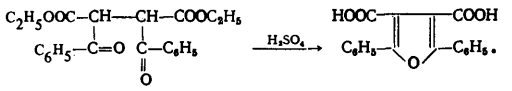


The sodium salt of the nitronic acid (VIII) underwent the Nef reaction under the influence of cold mineral acid[22] and was converted via the 1,4-dicarbonyl compound (IX) into esters of furan-3-carboxylic acid (X). By hydrolysing compound (X) and decarboxylating the acid, it is possible to obtain 2,3,5-trisubstituted furan derivatives.

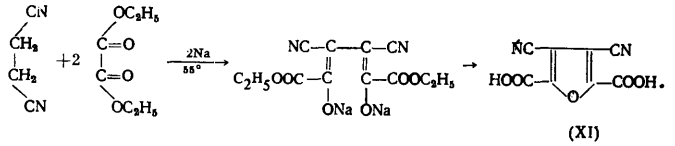
2. Syntheses from Saturated and Unsaturated 1,4-Diketones and 1,4-Keto-alcohols

The oldest method for the preparation of furan derivatives from aliphatic compounds is the cyclodehydration of the dienol forms of 1,4-diketones. As early as 1884, Bayer and Perkin[23] converted dibenzoylsuccinic ester into

2,5-diphenylfuran-3,4-dicarboxylic acid by refluxing for 20 h with 30% sulphuric acid:



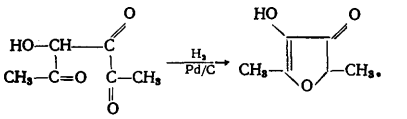
3,4-Diacetyl-2,5-dimethylfuran was obtained similarly by the action of hydrochloric acid on tetra-acetylethane [24,25]. In 1941 Trefil'ev and Lifanov [26] repeated this synthesis using hydrobromic acid. Subsequently an American patent was published, in which the preparation of the acid (XI) according to the scheme



(XI)

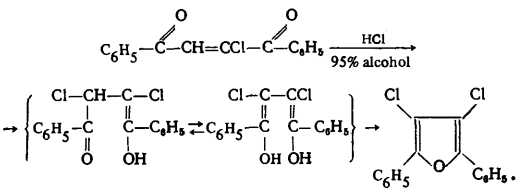
was described [27].

In 1956 Hoffmann and Eugster [28] synthesised the principal aromatic components of the pineapple fruit—3-hydroxy-2,5-dimethyl-4,5-dihydrofuran-4-one (XII):

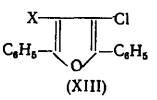


(XII)

The synthesis of tetrasubstituted furan derivatives from unsaturated 1,4-diketones was investigated in detail by Lutz and McGinn [29] using dibenzoylethylenes. They assumed that probably ring closure precedes the addition of the reagent in the 1,4-positions favouring cyclisation. Both *cis*- and *trans*-dibenzoylchloroethylenes react with hydrogen chloride in 95% alcohol forming 3,4-dichloro-2,5-diphenylfuran:



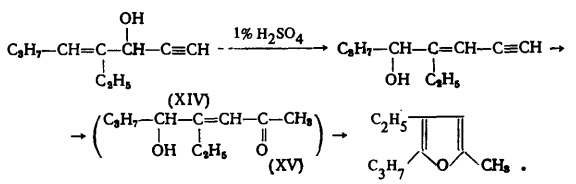
The reaction of *cis*-dibenzoylchloroethylene with acetyl chloride or acetic anhydride in the presence of sulphuric acid yields chloro- or acetoxy-furans (XIII):



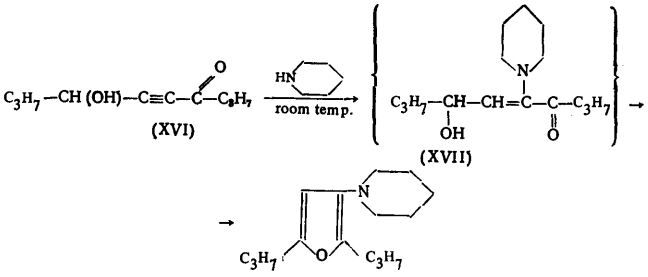
(XIII)

where X = Cl or $CH_3C(=O)-O-$.

Heilbron et al. [30] showed that enyne alcohols (XIV) are cyclised into a furan system during distillation with 1% sulphuric acid, probably via an intermediate keto-alcohol (XV):

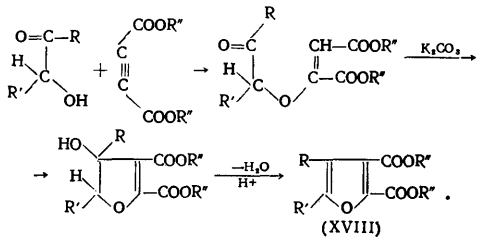


Cyclisation also takes place when piperidine is allowed to act upon the keto-alcohol (XVI), evidently also via an ethylenic 1,4-keto-alcohol (XVII):[31]



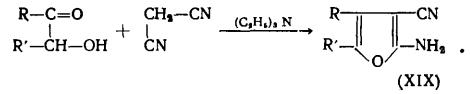
3. Other Syntheses of Aliphatic Compounds

Furan derivatives with the structure (XVIII) have been obtained by the condensation of the esters of acetylene-dicarboxylic acid with an α-hydroxy-ketone [32]:



(XVIII)

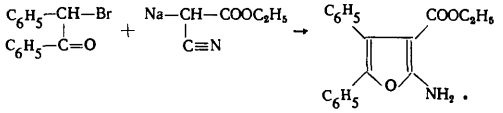
In 1966 Gewald [33] stated that the dinitrile of malonic acid readily reacts with α-hydroxy-ketones in the presence of bases, forming 2-amino-3-cyanofurans (XIX):



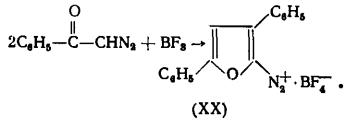
(XIX)

4-Acetyl-2-amino-3-cyano-5-methylfuran, analogous to compounds (XIX), had been synthesised earlier [34] from the dinitrile of malonic acid and 3-chloroacetylacetone. In contrast to the unsubstituted 2-aminofuran, these amino-furans are relatively stable. Only compounds (XIX) with a free α-position are sensitive to oxygen.

2-Amino-3-ethoxycarbonyl-4,5-diphenylfuran was obtained by the reaction of α-bromodeoxybenzoin with the sodio-derivative of cyanoacetic ester in ethanol [35]:



The first compound with a diazo-group in the furan ring, 2,4-diphenylfuran-5-diazonium fluoroborate (XX), was synthesised in 1963 by Reid and Bodenstedt [36], who allowed benzoyldiazomethane to react with boron trifluoride-ether:



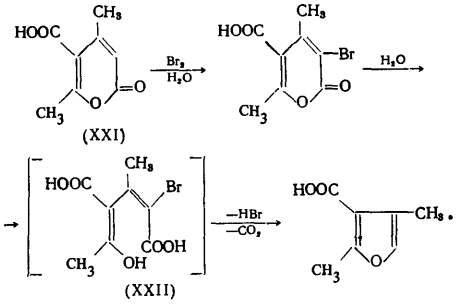
(XX)

It is noteworthy that the mechanisms of most of the reactions described above have an inadequate basis and the equations quoted must be regarded as only approximate.

The syntheses involve certain difficulties: frequently mixtures difficult to separate are formed and the yields of the desired products are as a rule low.

4. Syntheses from Other Cyclic Systems

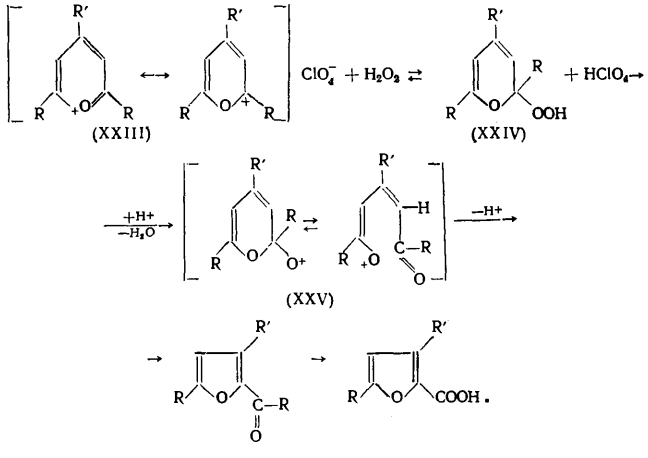
In his study of the bromination of α-pyrone derivatives Feist observed [37] that in some cases the reaction can be used to synthesise furan compounds. According to the suggested mechanism, dimethylcoumalic acid (XXI) gives rise to 2,4-dimethylfuran-3-carboxylic acid, probably via the intermediate (XXII):



(XXI)

(XXII)

In 1960 Balban and Nenitzescu [38] published a paper in which the synthesis of trialkyl-substituted furan derivatives from pyrylium salts is proposed. Earlier only one similar case of the contraction of the pyran ring in the hydrolysis of 2,4,5,6-tetraphenylpyrylium bromide had been described [39]. It was found [38] that, under the action of hydrogen peroxide, the readily available trialkylpyrylium perchlorates (XXIII) are converted into 3,5-dialkyl-2-acylfurans. These ketones were oxidised to the corresponding 3,5-dialkylfuran-2-carboxylic acids, whereby their structure was confirmed:



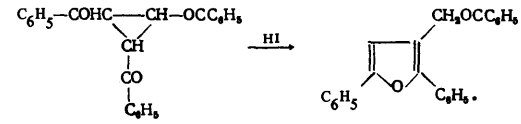
(XXIII)

(XXIV)

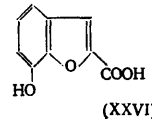
(XXV)

In this reaction the α-position of the pyran ring is subjected to nucleophilic attack by hydrogen peroxide and this gives rise to the peroxy-analogue of the pseudo-base (XXIV), which decomposes under the action of the acid formed. The formation of the furan ring favours the irreversible stabilisation of the cation (XXV).

Certain trisubstituted furan derivatives can be obtained from cyclopropane derivatives. For example, when concentrated hydriodic acid is allowed to act on *cis*- and *trans*-tribenzoylcyclopropanes, 2,5-diphenyl-3-phenylacetylfuran is formed [40]:

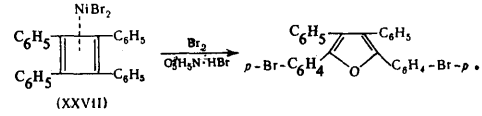


Furan-2,3,5-tricarboxylic acid was obtained from 7-hydroxycoumarone-2-carboxylic acid (XXVI) by oxidation with hydrogen peroxide in an alkaline solution [41]. In compound (XXVI) the benzene ring becomes sensitive to oxidation by virtue of the presence of the hydroxy-group, but the furan ring is stable [42] with respect to the action of hydrogen peroxide in an alkaline medium, particularly when it contains a carboxy-group:



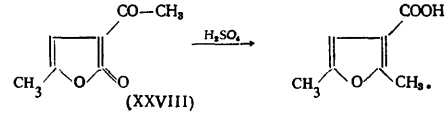
(XXVI)

Comparatively recently it has been established [43] that substituted furans may be obtained in high yield from the nickel bromide complex of tetraphenylcyclobuta-1,3-diene (XXVII) by treatment of the latter with bromine in the presence of pyridine hydrobromide which had been kept in moist air:



(XXVII)

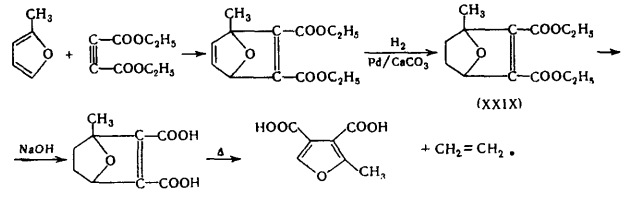
βγ-Unsaturated α-acyl-lactones can be readily converted into furancarboxylic acids. For example, 2,5-dimethylfuran-3-carboxylic acid is obtained smoothly from α-acetylangelicalactone (XXVIII):[44]



(XXVIII)

5. Preparation from α-Monosubstituted Furan Derivatives by Successive Diene and Retrodiene Syntheses

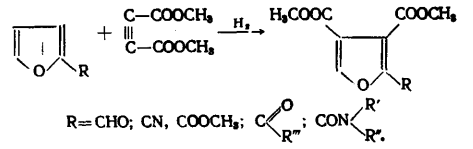
Adler and Rickert [45] showed that the adduct obtained by the addition of the diester of acetylenedicarboxylic acid to silvan can be partially reduced with hydrogen over a palladium catalyst. The product (XXIX) is converted into 2-methylfuran-3,4-dicarboxylic acid on hydrolysis and heating (retrodiene synthesis):



(XXIX)

Similarly the corresponding 2,3,4-trisubstituted furan derivatives were obtained from 1-acetamido-1-(fur-2′-yl)-ethane [46] and the acetal of furfural [47]. Recent investigations [48,49] revealed the capacity of furan derivatives substituted in the α-position by electron-acceptor groups to

react as dienes with the dimethyl ester of acetylenedicarboxylic acid:

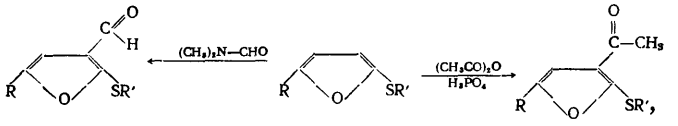


The method of consecutive diene and retrodiene syntheses is used[50] to identify the α- and β-furyl residues in natural products since furan-3,4-dicarboxylic acid is formed from mono-β- or $\beta\beta'$-disubstituted derivatives[51,52] as a result of the reactions described above, while mono-α-derivatives yield trisubstituted furan.

6. Substitution Reactions of α-Monosubstituted Furan Derivatives

The vast majority of known trisubstituted furan derivatives have been obtained by the electrophilic substitution of readily available mono-α-substituted furans: silvan, furfural, and pyromucic acid and its esters. It is generally known that, regardless of its nature, a new substituent enters into the second α-position in the ring of an α-monosubstituted furan. The possibility of further substitution in the β-position depends on the type of substituents already present in the α- and α'-positions and on the nature of the attacking reagents.

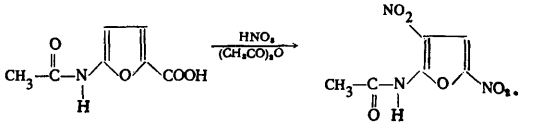
If the α-positions of the ring are substituted by two identical electron-donor groups, the introduction of a third substituent, although possible, is hindered as a result of the competing reaction involving the opening of the furan ring or the displacement of one of the existing groups by the attacking reagent[53]. For example, 2,5-dimethylfuran may be nitrated[54], chloromercurated[55], sulphonated[56], and acylated[7] in the β-position, but it does not undergo the Gattermann–Koch reaction[57]. In this case the ring is opened and acetonylacetone is formed. For furan derivatives with two electron-donor non-identical substituents in the α-position, only isolated examples of the introduction of β-substituents are known, since the reaction is usually accompanied by the opening of the furan ring. Examples are the acylation and formylation of 2-alkyl-5-alkylthiofurans (XXX).[58] The new substituent occupies the β-position adjacent to the alkylthio-group:



(XXX)

where R and R′ = alkyl.

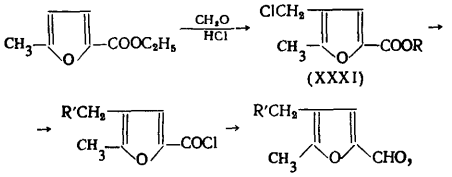
Examples of the formation of trisubstituted furan derivatives when the α- and α'-positions of the ring are occupied by different electronegative groups are encountered rarely; in the main they occur with compounds having two identical electron-acceptor groups. For example, the diethyl ester of furan-2,5-dicarboxylic acid can be mercurated[59] and chlorinated[60] but not brominated[61–63]. Furan-2,5-dicarboxylic acid is inert with respect to reagents such as aqua regia, fuming nitric acid, bromine, and concentrated sulphuric acid[55]. The greatest number of β-substitution reactions is known for $\alpha\alpha'$-disubstituted furans in which one group is an electron donor and the other an electron acceptor. These are mainly substituted esters of furan-2-carboxylic acid[64–77]. The work of Sasaki[78] on the nitration of 2,5-disubstituted furan derivatives with substitution should be mentioned:



The replacement of the carboxy-group by a nitro-group takes place with best yields in the case of electron-donor groups in the α'-position of the furan ring.

The introduction of two substituents into the furfural molecule[79] or silvan molecule[56,80,81] has been described, but such cases are rare; they include, in particular, the syntheses[82,83] of 4,5-dibromofurfural and 2-acetyl-4,5-dibromofuran in one stage using aluminium chloride without solvent. Under the conditions of the bromination of furfural[84] or its acylal[85,86] in a solvent without aluminium chloride, 5-bromofurfural is formed. Apart from the procedures described above, there are also others leading to trisubstituted furans, for example from 3,4-disubstituted[87,88], 2,3-disubstituted[88,89], and 2,4-disubstituted[79,90,91] derivatives, but these are of limited applicability.

A series of papers dealing with the synthesis of new tri- and tetra-substituted furan derivatives via the reactions of groups already present in the furan ring have been published. Among these one should mention the investigation of Mndzhoyan et al. of the synthesis of the chloroacetyl-, β-chloropropionyl-, and p-nitrobenzoyl-amides of 4,5-disubstituted furan-2-carboxylic acid[95] and of the preparation of the ethyl ester of 4-chloromethyl-5-methylfuran-2-carboxylic acid[67] (XXXI) and its conversion into 4,5-dimethylfuran-2-aldehyde[68], 5-bromoethyl-4-chloromethylfuran-2-carboxylic acid[92], 2-dimethylaminoethyl ester of 4-benzyl-5-methylfuran-2-carboxylic acid[92], and 4-benzyl-5-methylfuran-2-aldehyde[94], from which the nitrile, amide, and amine were obtained:



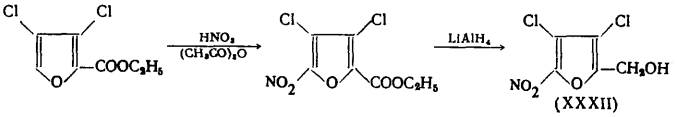
(XXXI)

where R = H or C_2H_5 and R′ = H or C_6H_5.

Janda and coworkers[96,97] synthesised the methyl ester (XXXI) from 5-acetylsilvan and replaced the chloromethyl group by an aldehyde group.

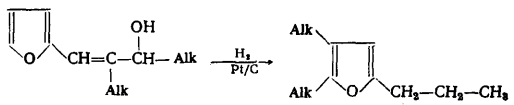
In a study of the possibility of the allyl rearrangement in certain tetrasubstituted furans, for example in 3,4-dichloromethyl-2,5-dimethylfuran under the action of sodium cyanide, Novitskii et al.[98] obtained certain new tetrasubstituted furans. They also synthesised[99] a number of trisubstituted furans.

Michels[100] described the conversion of the ester of 3,4-dichlorofuran-2-carboxylic acid into the alcohol (XXXII):

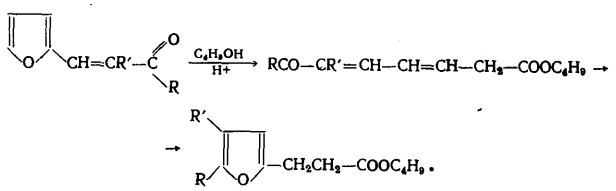


(XXXII)

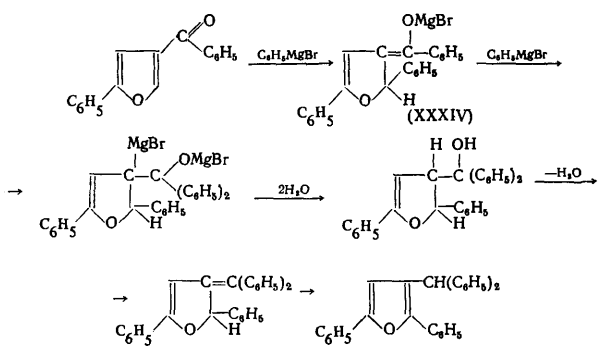
There exist patent data[101] concerning the synthesis of trialkylfurans (XXXIII) by a procedure involving a catalytic hydrogenation stage over platinum:



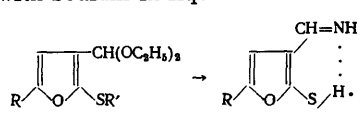
Esters of 4,5-dialkylfuran-2-propionic acids were obtained from fur-2-ylalkenones by acid-catalysed alcoholysis[102]:



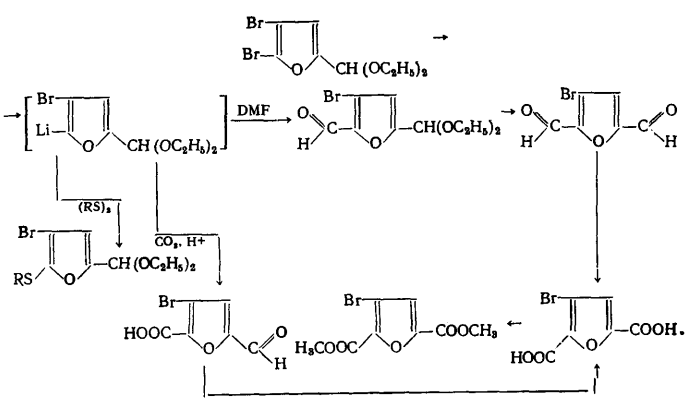
An example of the synthesis of a trisubstituted furan from a 2,4-disubstituted derivative, 4-benzoyl-2-phenylfuran, has been described[103]. In this case probably one phenylmagnesiumbromide molecule adds initially to the 1,4-positions of the conjugated system and the second molecule to the double bond of compound (XXXIV):



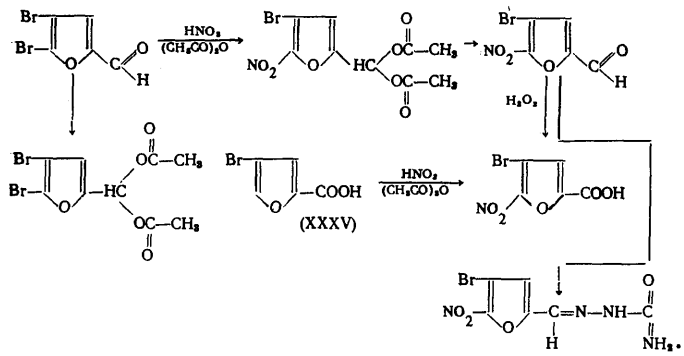
Like the corresponding acetals of the thiophen series[104], the acetals of 5-alkyl-2-alkylthiofuran-3-aldehydes are converted[105] into 5-alkyl-2-mercaptofurfurylideneimines on treatment with sodium in liquid ammonia:



By virtue of the inertness of the acetalised aldehyde group to the action of butyl-lithium, it proved possible to synthesise from 4,5-dibromofuran-2-aldehyde[82,83] the previously unknown sulphides, dialdehydes, and diesters with a bromine atom in the β-position of the ring[106]:



New nitro-derivatives, which may prove of interest as antibacterial agents, were also obtained by the substitution of a bromine atom in the α-position by a nitro-group[106]. The substitution of bromine in the α-position[84,107] by a nitro-group in the furan series is not always possible.



It is noteworthy that the present authors were able to nitrate the acid (XXXV) with formation of 4-bromo-5-nitrofuran-2-carboxylic acid. Judging from the literature data[72], in the nitration of compound (XXXV) the furan ring cleaves to form bromofumaric acid.

III. METHODS OF SYNTHESIS OF MONO-β-SUBSTITUTED FURAN DERIVATIVES

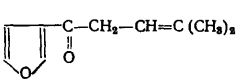
The information about the preparation of β-monosubstituted furan derivatives is extremely limited; this is undoubtedly because of the difficulties associated with their synthesis. In fact up to 1933 not a single mono-β-substituted furan had been obtained. Only isolated cases of the introduction of a substituent in the β-position of an unsubstituted furan molecule were described. When furan is alkylated with propene in the presence of boron trifluoride-ether, a very small amount of the isomeric mono-β-alkyl derivative is formed together with the α-isomer[108]. By alkylating furan with isobutene and pentene in the presence of phosphoric acid on kieselguhr, it is possible to obtain[109] β-alkylfurans with acceptable yields, but containing an admixture of α-isomers. It is interesting to note that 2-t-butylfuran isomerises[109] over this catalyst to 3-t-butylfuran. Nevertheless these data have no value when the aim is to synthesise β-monosubstituted furans.

We shall now examine the methods available at present for the preparation of β-monosubstituted furan derivatives.

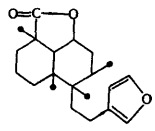
1. Isolation from Natural Products

The first known 3-monosubstituted furan, furan-3-carboxylic acid, was not synthesised but was isolated from plants[110,111]. The principal component of perilla oil is 3-furyl isopentyl ketone[112,113]. The oil also contains 3-(4'-methylpent-3'-enyl)furan[113,114]. Each year there is an increase in the number of β-monosubstituted furan derivatives discovered as constituents of natural materials[50,115-118].

In 1962 a ketone with the following structure was obtained from perilla oil[119]:

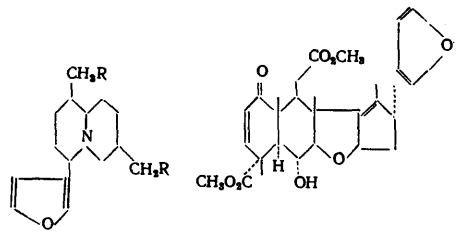


The following structure has been proposed for marrubiin, which incorporates a non-condensed 3-substituted furan ring[120]:

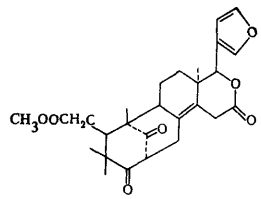


The structure of this compound was confirmed[121] by additional data.

It is suggested[122,123] that the β-furyl residue is a structural component of the castoramine molecule and "nimbinic acid", to which the following structures are attributed respectively:

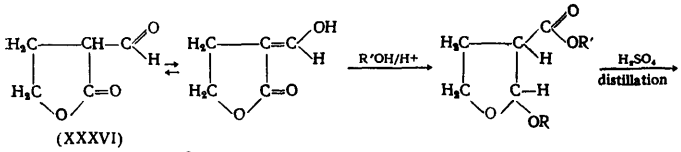


The following structure has been assigned to mexicanolide, a natural lactone[124]:

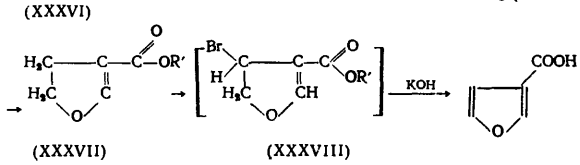


2. Cyclisation of Aliphatic Compounds

There are very few examples of the preparation of β-monosubstituted furan derivatives by direct ring closure of aliphatic compounds. The method of synthesis of furan-3-carboxylic acid, proposed fairly recently, is interesting. α-Formyl-γ-butyrolactone (XXXVI) is obtained from the readily available γ-butyrolactone formed[125] by the dehydration of butane-1,4-diol and subsequent condensation with formic ester[44]:

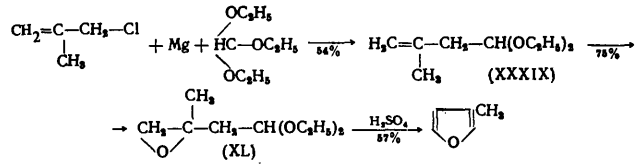


(XXXVI)

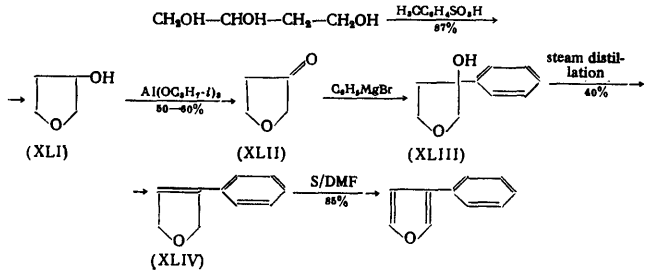


(XXXVII) (XXXVIII)

The rearrangement[44] of this lactone to the ester of 4,5-dihydrofuran-3-carboxylic acid (XXXVII) and bromination[126] of the latter by *N*-bromosuccinimide leads to an unstable product (XXXVIII), which is converted by treatment with aqueous alkali into furan-3-carboxylic acid with 58% yield[126]. A convenient three-stage synthesis of 3-methylfuran has been described[127]. The diethyl acetal of 3-methylbut-3-enal (XXXIX), formed by the reaction of methylallyl chloride, magnesium, and orthoformic ester, is converted by oxidation with perphthalic acid into the epoxide (XL), the hydrolysis of which yields 3-methylfuran:



Wynberg[128] synthesised 3-phenylfuran from 1,2,4-trihydroxybutane:



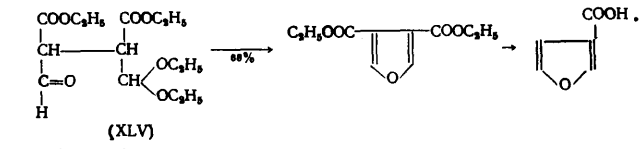
Compounds (XLI), (XLII), and (XLIII) were obtained for the first time by Yur'ev and Korobitsyn[129,130].

The last stage in the conversion of 3-phenyl-2,5-dihydrofuran (XLIV) into 3-phenylfuran, in 2–3% solution of sulphur in dimethylformamide, requires special attention. When 3-hexyl-2,5-dihydrofuran is treated similarly[128] with a solution of sulphur in dimethylformamide, the expected results are not achieved. This method is particularly interesting, since the attempt[128] to prepare 3-phenylfuran from 3-phenylfuran-2-carboxylic acid, synthesised by a standard method[131], proved unsuccessful.

3. The Removal of Two or One Substituents from Tri- and Di-substituted Furan Derivatives

The structure of furan-3-carboxylic acids isolated from a natural product was confirmed in 1932 by Reichstein[132], who obtained it by the decarboxylation of furan-2,3-dicarboxylic acid (see p. No. 401). A year later Reichstein prepared it[133] by the decarboxylation of furan-3,4-dicarboxylic acid. When furantetracarboxylic acid is heated to 270°C, furan-2,3,4-tricarboxylic and furan-3,4-dicarboxylic acids are formed. On heating with copper in quinoline, the latter yields furan-3-carboxylic acid.

Gilman showed[134] that furan-3-carboxylic acid can be obtained by the decarboxylation of furan-2,4-dicarboxylic acid. In connection with the development[135] of a relatively simple method for the synthesis of furan-3,4-dicarboxylic acid, consisting in the cyclisation of the diethyl ester of 2-diethoxymethyl-1-formylsuccinic acid (XLV), there arose the possibility of the direct synthesis[136] of furan-3-carboxylic acid:

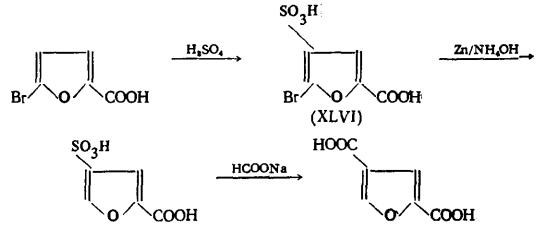


(XLV)

Probably this method is the most convenient preparative procedure.

3-Methylfuran has been obtained[19,20] by the decarboxylation of 4-methylfuran-2,3-dicarboxylic acid and also 3-methylfuran-2-carboxylic acid[131,137,138].

3-Nitrofuran was prepared by Rinkes[65] from 5-methyl-4-nitrofuran-2-carboxylic acid. Its decarboxylation yielded[77] 2-methyl-3-nitrofuran, which was oxidised to 4-nitrofuran-2-carboxylic acid, the latter being decarboxylated to 3-nitrofuran in 18% yield. Furan-3-sulphonic acid was also obtained[139] by the elimination of substituents from the α-positions of a trisubstituted furan, namely 5-bromo-4-sulphofuran-2-carboxylic acid (XLVI). The latter was synthesised for the first time by Hill and Palmer[140] by treating 5-bromofuran-2-carboxylic acid with fuming sulphuric acid. However, they did not establish which of the two β-positions was substituted by the sulpho-group. The structure of the acid (XLVI) was confirmed by Gilman[69] by means of reactions leading to the formation of the known furan-2,4-dicarboxylic acid:

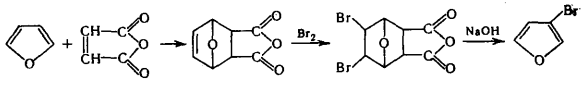


Treatment of compound (XLVI) with an equimolar amount of bromine by a standard method[141] yielded 2,5-dibromofuran-3-sulphonic acid[139], which was converted into furan-3-sulphonic acid by Hills method[140].

β-Halogenofurans may be obtained[53,142] by the removal of three halogen atoms from tetrahalogenofurans. However, this method cannot be regarded as convenient because of the difficulty of synthesising the starting materials and because the reaction products are obtained in low yields. 3-Bromofuran and 3-chlorofuran were obtained[143] from 4,5-dibromo-, 4,5-dichloro-, and 3,4-dichloro-furan-2-carboxylic acids by the action of zinc in aqueous ammonia followed by decarboxylation in quinoline in the presence of copper.

Certain doubts have been expressed about the method of preparation of 3-bromofuran[144]. They concerned the reproducibility of the yields in the bromine elimination stage. Consequently Gronowitz and Sorlin suggested that 3-halogenofuran, namely 3-iodofuran, be obtained from furan-2-carboxylic acid via 3-chloromercurifuran (see p. 397).

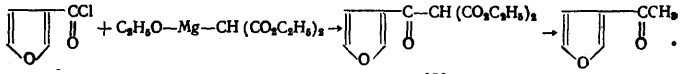
There exist also other indirect methods for the introduction of a halogen into position 3 of the furan ring, for example by the bromination of the adduct of furan and maleic anhydride[145]:



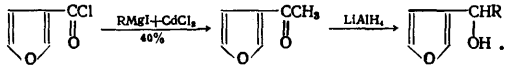
4. Syntheses Based on Furan-3-carboxylic Acid

Among the β-derivatives of furan, furan-3-carboxylic acid is the most readily available and the most frequently used starting material in various syntheses. The preparation from it of 2,4-disubstituted furan derivatives is described below (see p. 399). The syntheses of a number of β-monosubstituted furan derivatives, consisting in the conversion of the carboxy-group, will be examined here. Gilman obtained[134] furan-3-aldehyde by the Rosenmund reduction of the chloride of furan-3-carboxylic acid and the reduction of furan-3-aldehyde by the Wolff–Kishner method gave 3-methylfuran. Monosubstituted β-ketones, individual representatives of which are encountered in natural products[112,113,119], remained inaccessible for a very long time. Information[146] about their preparation included no data concerning the experimental conditions and the constants and analyses of the desired products. This made it difficult for other investigators to repeat the syntheses[147].

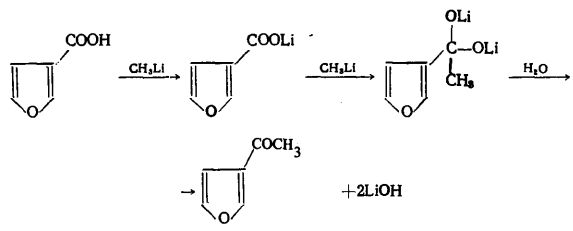
Kubota and Naya[148] obtained in 1956 3-acetylfuran in 86% yield by the Reynolds method[149] from the chloride of furan-3-carboxylic acid:



In 1959 Grunanger and coworkers[150] synthesised in low yields a number of alkyl 3-furyl ketones by the reaction of the chloride of furan-3-carboxylic acid with organocadmium compounds. The ketones were reduced to the corresponding alcohols in high yields:

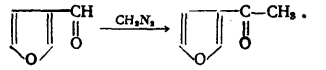


Somewhat later Gronowitz and Sorlin[147] obtained 3-acetylfuran from furan-3-carboxylic acid by Tegner's reaction[151] consisting in the interaction of methyl-lithium with carboxylic acids:

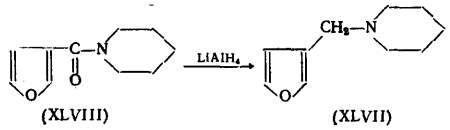


The constants of 3-acetylfuran (a crystalline compound) and its semicarbazone, quoted in these papers, agree, but differ from the data of Gilman et al.[146], who described 3-acetylfuran as liquid.

The work of Capuano[152], which has hardly any preparative value for the synthesis of 3-acetylfurans because its yield is too low, should also be mentioned:



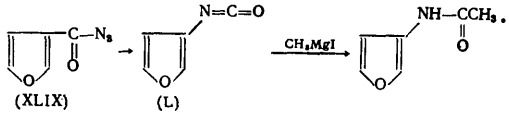
In connection with studies on the alkaloids of the yellow lily, *N*-(fur-3′-ylmethyl)piperidine (XLVII) was synthesised[136] by the reduction of *N*-(3-furoyl)piperidine (XLVIII):



(XLVIII) (XLVII)

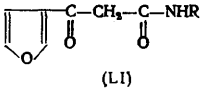
The history of one synthesis based on furan-3-carboxylic acid, namely the preparation of 3-acetamidofuran, is interesting. When this investigation was undertaken[153], the author could hardly suppose that subsequently it might prove to be of value for the demonstration of the structure

of a natural product. It was found that, when *N*-acetyl-D-glucosamine and *N*-acetyl-D-galactosamine, which form part of the polysaccharides of chitin and cartilage, were treated[154] with a solution of sodium carbonate, furan compounds were formed, one of which is 3-acetamidofuran. Its structure was confirmed[155] synthetically by repeating the Burtner synthesis[153]. Furan-3-carboxylic acid was converted into its chloride in 60% yield. Under the conditions specified by Naegeli and Stefanovitsch[156], the latter reacted with sodium azide to give 3-furoyl azide (XLIX) in 80% yield. Subsequently this azide was subjected to the Curtius rearrangement and was converted in 60% yield into the isocyanate (L), from which 3-acetamidofuran was obtained in 41% yield by the action of methylmagnesium iodide:



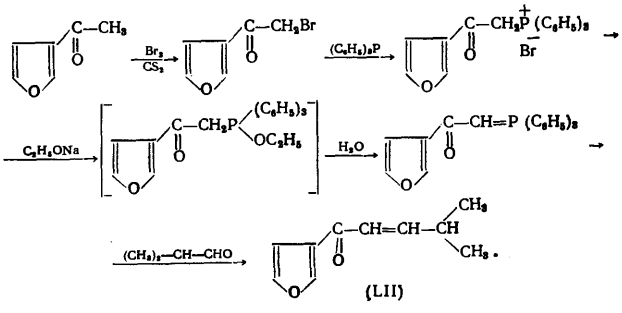
(XLIX) (L)

Starting from furan-3-carboxylic acid, Wul'fson and Kolchin[157] synthesised the substituted amides (LI) of 3-furoylacetic acid:



(LI)

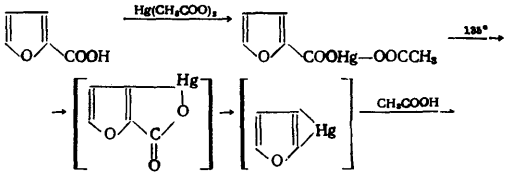
The synthesis of the ketone (LII) should also be mentioned[158]:

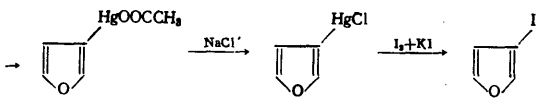


(LII)

5. Syntheses Based on Furan-2-carboxylic Acid

In 1933 Gilman and coworkers[53] showed that the reaction of mercuric chloride with the sodium salt of pyromucic acid results in decarboxylation, the chloromercuri-group entering the furan ring. When mercuric acetate is allowed to act on pyromucic acid under the conditions described by Pesci[159] with subsequent pyrolysis of the resulting mixed salt, 3-acetoxymercurifuran is obtained instead of the expected 2-acetoxymercurifuran. Thus here we are dealing with the *ortho*-rearrangement characteristic of aromatic mercury salts, although the reaction is in this case more complex and its mechanism cannot be regarded as established:





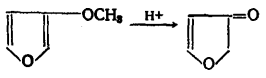
This synthesis is interesting because it permits the introduction of a substituent into the β-position of the furan ring, while leaving the α-positions free. In furan-3-carboxylic acid the carboxy-group cannot be replaced by the chloromercuri-group. The yield of 3-chloromercurifuran amounts to 15%, which was recently comparatively confirmed by other investigators[147,160], 3-Chloromercurifuran is an infusible compound insoluble in all solvents, which can be converted by treatment with an aqueous solution of iodine and potassium iodide into 3-iodofuran in 46% yield. Gilman also noted[53] that the attempt to prepare 3-acetylfuran by the action of acetyl chloride on 3-chloromercurifuran was unsuccessful. Gilman characterised 3-iodofuran as a much more stable compound than 2-iodofuran; it was shown that the iodine in this compound is not very labile. 3-Iodofuran did not react even with activated magnesium or lithium and underwent only partial exchange for the metal when acted upon by a sodium–potassium alloy.

The reactions of 3-chloromercurifuran were investigated in greater detail fairly recently by Gronowitz and Sorlin[147,160], who found that it is impossible to obtain 3-substituted furan derivatives by treating 3-chloromercurifuran with bromine, thiocyanogen, or acetyl chloride in benzene solution. In bromination experiments it was impossible to isolate the reaction products but it was established that the substitution takes place at a carbon–hydrogen bond and not an organometallic bond. Treatment with thiocyanogen gave a low yield of a mixture of 2- and 3-isomers in proportions of 4 : 1, which the authors also explained by the competition of reactions at the C–H bond in the active α-position and the C–Hg bond at the β-position in the ring. The product of the interaction of 3-chloromercurifuran with acetylchloride in benzene is 2-acetylfuran (yield 17%). Consequently 3-substituted furan derivatives can be obtained from 3-chloromercurifuran only by reaction with iodine and, as established by Bak et al.[161], with deuterium chloride.

The fact that in some cases an electrophilic agent attacks the reactive α-position of the five-membered heterocyclic compound more readily than the organometallic bond in the β-position was first discovered in the thiophen series. Namely, Gronowitz found[144] that, when 3-thienyl-lithium was acted upon by cadmium chloride and zinc chloride with subsequent treatment with acetyl chloride, a mixture of 55% of 2-acetylthiophen and 31% of 3-acetylthiophen was obtained.

Gronowitz and Sorlin also confirmed[147] and improved Gilman's results; in experiments designed to synthesise 3-iodofuran it proved possible to increase the yield from 46 to 75%; the scope of syntheses based on 3-iodofuran was also extended. In particular, it was shown that the iodine atom in 3-iodofuran is not as inert as was suggested by Gilman. It is sufficiently labile to undergo exchange for lithium in the reaction with alkyl-lithium in ethereal solution at −70°C. This permits the synthesis of new 3-substituted furan derivatives. When carbon dioxide, *NN*-dimethylformamide, and dimethyl disulphide were allowed to react with this organolithium compound, furan-3-carboxylic acid (yield 72%), furan-3-aldehyde (yield 38%), and fur-3-yl sulphide (yield 75%) were obtained respectively. Furthermore, it was shown[147] that, in contrast to 2-bromo- and 2-iodo-furan[162], 3-iodofuran

reacts with sodium methoxide in methanol in the presence of copper(II) oxide, forming 3-methoxyfuran in 65% yield. 3-(2*H*)-furanone (LIII) was synthesised by the acid hydrolysis of 3-methoxyfuran [163]:



(LIII)

The reaction of 3-iodofuran with copper cyanide in quinoline gave [147] 3-cyanofuran in 50% yield.

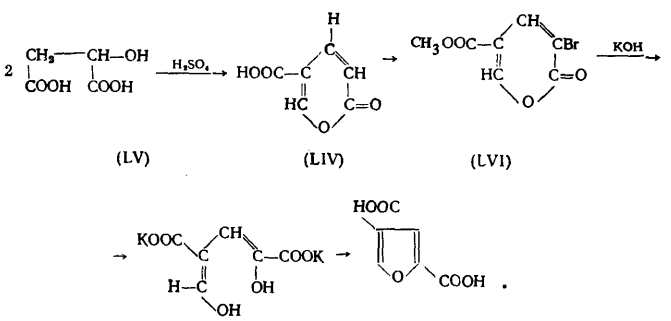
IV. METHODS OF SYNTHESIS OF 2,4-DISUBSTITUTED FURAN DERIVATIVES

The methods discussed below are mainly used to obtain 2,4-disubstituted furan derivatives.

1. Cyclisation of Certain Aliphatic Compounds

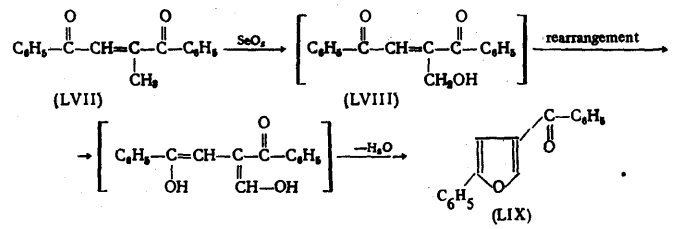
2,4-Disubstituted furans of various types are difficult to obtain, since the second electrophilic substituent usually enters the α'-position in the ring, forming 2,5-disubstituted furans regardless of the directing capacity of the group already present in the α-position. Only one rather difficult to explain case is known where in the reaction of isopropyl chloride with furfural in the presence of aluminium chloride the alkyl group enters the β'-position [79,164,165] (yield of 4-isopropylfurfural 11%). However, this is not a typical example and there is no doubt that it cannot be classified as a general method for the synthesis of 2,4-disubstituted furan. Usually, in order to obtain 2,4-disubstituted furans as well as the mono-3-substituted derivatives and 2,3-disubstituted derivatives, it is necessary to use rather inefficient "indirect" procedures. One of these is cyclisation by a suitable method of selected aliphatic compounds, the synthesis of which is often associated with considerable difficulties. We shall quote as an example the synthesis of furan-2,4-dicarboxylic acid [134] from malic acid via coumalic acid.

There exist also other methods [41] for the preparation of this acid, but they are used more rarely. Gilman [134] obtained coumalic acid (LIV) from malic acid (LV) by Pechman's synthesis [166], consisting in the treatment of malic acid with sulphuric acid; the acid (LIV) was then obtained in 60% yield. The methyl ester of the acid was further converted by the Feist reaction [167] into the ester of bromocoumalic acid (LVI) in 65% yield and the latter into furan-2,4-dicarboxylic acid in 50% yield:



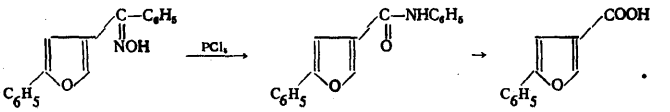
(LV) (LIV) (LVI)

The cyclisation of 1,2-dibenzoylprop-1-ene (LVII) in its oxidation with selenium dioxide also leads [168] to a 2,4-disubstituted furan—4-benzoyl-2-phenylfurfuran. The authors [168] suggest that initially the methyl group at the double bond is oxidised to an alcoholic group and the ketone (LIX) is formed from the alcohol (LVIII) as a result of a prototropic rearrangement with subsequent elimination of water:

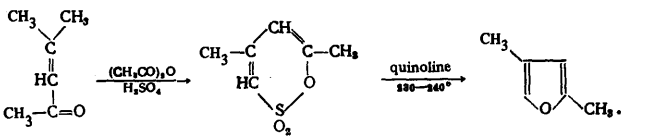


(LVII) (LVIII) (LIX)

The same workers [168] achieved the Beckmann rearrangement of the ketone oxime, which leads to 5-phenylfuran-3-carboxylic acid, a compound otherwise difficult to obtain:

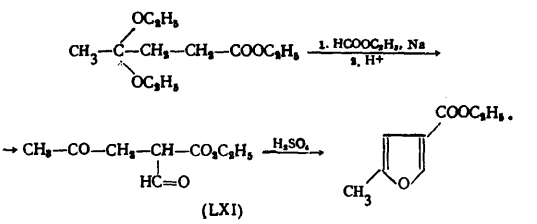


In 1948 Morell proposed [169] a novel synthesis of 2,4-disubstituted furans consisting in the heating of 3,5-dimethylsultone (LX) in quinoline. However, in view of the low availability of compound (LX) (low yields), this method can hardly be regarded as preparative:



(LX)

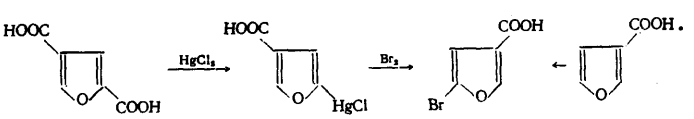
The synthesis of 5-methylfuran-3-carboxylic acid from levulinic acid [170] consists in the condensation of the diethyl ketal of levulinic acid with formic ester and subsequent cyclisation of the ester (LXI) by treatment with sulphuric acid:



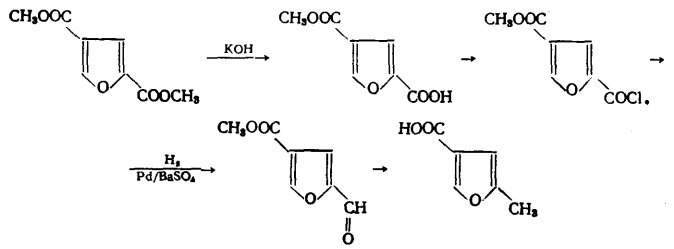
(LXI)

2. Reactions of Furan-2,4-dicarboxylic Acid

Despite the difficulties in its preparation, furan-2,4-dicarboxylic acid is regarded as the most readily available in the series of 2,4-disubstituted furans. A number of other 2,4-disubstituted derivatives were obtained by the conversion of its carboxy-groups. For example, by selective substitution of the α-carboxy group by a chloromercuri-group, Gilman and Burtner synthesised [134] 2-bromofuran-4-carboxylic acid in order to confirm the structure of the product formed on bromination of furan-3-carboxylic acid:

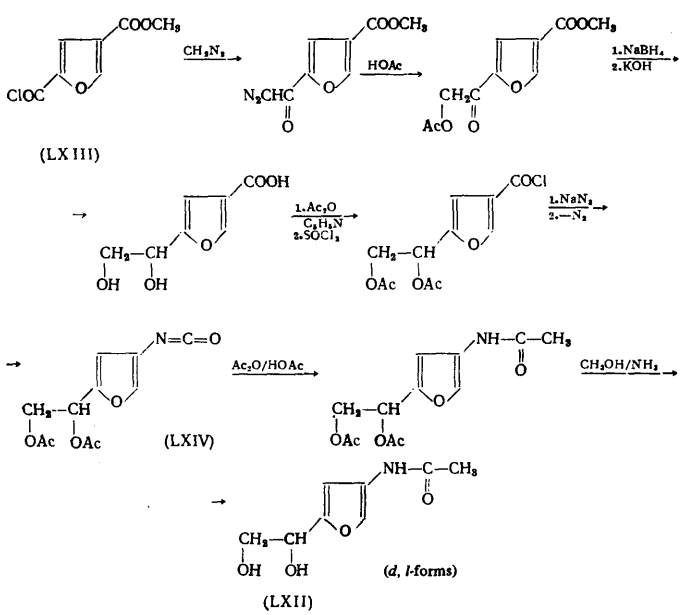


5-Methylfuran-3-carboxylic acid was also obtained[171] from furan-2,4-dicarboxylic acid:



This method is based on the more ready hydrolysis of the ester group of the diester in the α-position.

The difficulties which must be overcome in the synthesis of 2,4-disubstituted furans may be demonstrated by means of the following example: in order to confirm[154] the structure of "chromogen III" (LXII), isolated from natural products (chitin and the polysaccharides of cartilage), it was necessary to undertake a seven-stage synthesis. The seven stages, starting with malic acid and proceeding via coumalic and furan-2,4-dicarboxylic acids to the chloride of 4-methoxycarbonylfuran-2-carboxylic acid (LXIII), were described earlier[171]. Further stages[154] are illustrated by the following scheme:



In this synthesis the isocyanate (LXIV) was converted into 3-acetamido-5-diacetoxyethylfuran by a standard method[172] —by the action of a 1:1 mixture of acetic anhydride and acetic acid.

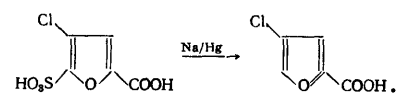
3. Electrophilic Substitution Reactions in the Series of Furans Substituted in the β-Position by *Meta*-directing Groups

Reactions of this kind are extremely rare. In 1933 Gilman[134] formulated the directing rule operating when a substituent enters the furan ring with an electronegative group in the β-position. For the nitration and bromination of furan-3-carboxylic acid and also furan-3-aldehyde as examples, it was shown that the site of substitution is the further removed α-position in the ring, as a result of which 2,4-disubstituted furans are produced.

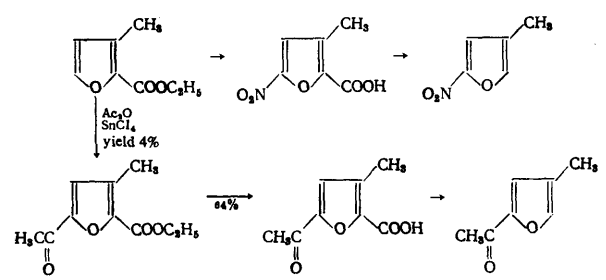
4. Elimination of One Substituent from Trisubstituted Furans

Probably the most widely used procedure employed in the synthesis of 2,4-disubstituted furans is the removal of certain groups, usually halogen atoms[62,69-71,73,74] and a carboxy-group[41,81,173] from trisubstituted furans. The reagents most often used to eliminate halogen atoms are zinc in acetic acid, alcoholic ammonia, or aqueous ammonia solutions, and sodium amalgam.

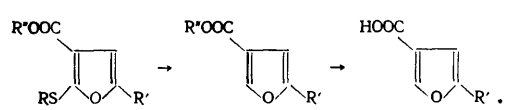
An example of the synthesis of a 2,4-disubstituted furan, namely 4-chlorofuran-2-carboxylic acid, by the elimination[70] of a sulpho-group has also been described:



It is noteworthy that 4-methyl-2-nitrofuran[81] and 2-acetyl-4-methylfuran[173] were obtained via a trisubstituted derivative starting with the relatively readily available 2,3-disubstituted derivative:

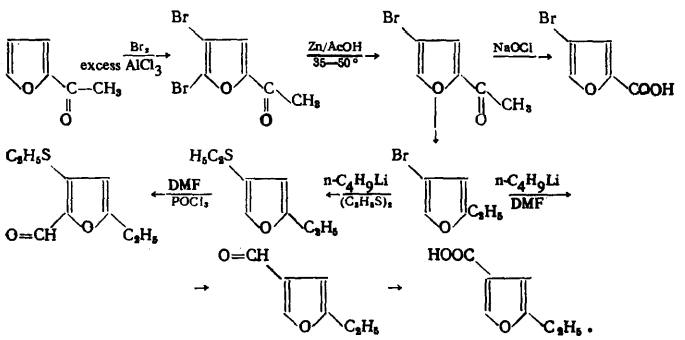


Recently a series of 2,4-disubstituted furans were prepared[58,174] by the elimination of a sulphide group from trisubstituted furans with the aid of Raney nickel:



The authors of the present review demonstrated for the first time the possibility of eliminating sulphide sulphur from furan derivatives by Raney nickel with preservation of the ring double bonds in the synthesis of 2,3-disubstituted furans[175] and proposed a method for the selective elimination of a bromine atom from the α-position in 2-acetyl-4,5-dibromofuran with zinc in acetic acid[176]. Under the conditions discovered, the keto-group and the bromine atom in the β-position do not undergo any changes. We were unable to find any literature data concerning the possibility of the elimination of a halogen atom from the furan ring while retaining the carbonyl group. Usually the latter, in particular in an aldehyde, is reduced to an alcoholic or a methyl group under the action of zinc in acetic acid[177] (a modification of the Clemmensen reaction).

Only Lutz and coworkers mention in one of their communications [178] the elimination by zinc in acetic acid of two bromine atoms from 3-(ω-dibromoacetyl)-2,5-diphenylfuran with retention of the keto-group. 2-Acetyl-4-bromofuran, which we obtained, is a key compound for the synthesis of many 2,4-disubstituted furans (bromides, sulphides, etc.):

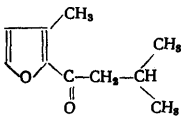


V. METHODS OF SYNTHESIS OF 2,3-DISUBSTITUTED FURAN DERIVATIVES

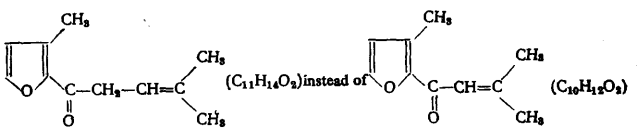
The known 2,3-disubstituted furans were obtained from certain natural products, by the cyclisation of aliphatic compounds into a furan system, the conversion of the carboxy- or methyl groups in 2-methylfuran-3-carboxylic and 3-methylfuran-2-carboxylic acids, by the elimination of one substituent from trisubstituted furans, mainly by the decarboxylation of acids, and by substitution of the available β-monosubstituted furans, mainly 3-methylfuran.

1. Isolation from Natural Products

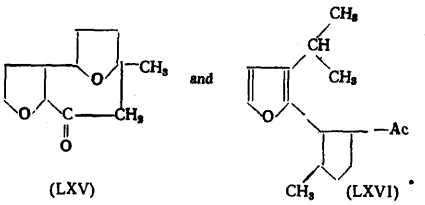
Most of the furan compounds encountered in nature are terpenoids [179]. Together with mono-β-substituted derivatives, a number of 2,3-disubstituted furans were isolated from natural products: 2-isovaleroyl-3-methylfuran [180],



"naginata ketone", and others. The "naginata-ketone" was detected for the first time in the essential oil of *Elsholtzia oldhami* by Fujita [181], who incorrectly attributed to it the structure

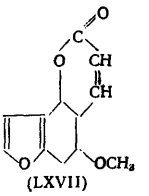


as established by Naves and Ochsner [182]. The structures of ipomeamarone [183] (LXV) and pelargone [184] (LXVI) from the essential oil of *Bourbon geranium*, which are also 2,3-disubstituted furan derivatives, were likewise elucidated:

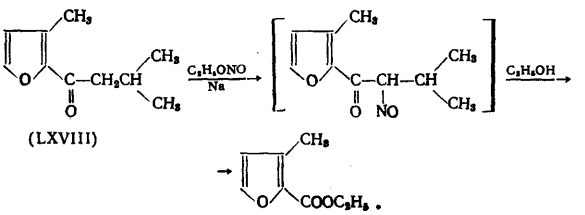


Isomaltol, isolated for the first time from bread by Back [185] and obtained recently by Hodge and coworkers [186] by appropriate treatment of lactose, is also a 2,3-disubstituted furan, namely 3-hydroxyfur-2-yl methyl ketone, as shown by Fischer and coworkers [187].

A substance called isobergaptene (LXVII) was isolated from the roots of *Pimpinella saxifraga* [188]. Its oxidation with hydrogen peroxide in alkaline solution gave furan-2,3-dicarboxylic acid:

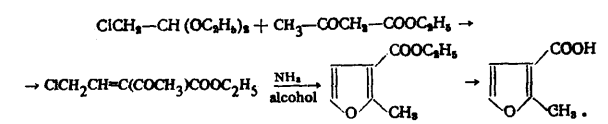


When ethyl nitrite and sodium were allowed to react with isobutyl 3-methylfur-2-yl ketone (LXVIII), isolated from the essential oil of a member of the labiatae (*Elsholtzia Cristata wild*), the ketone decomposed with formation of the ester of 3-methylfuran-2-carboxylic acid [137]:



2. Cyclisation of Aliphatic Compounds into the Furan System

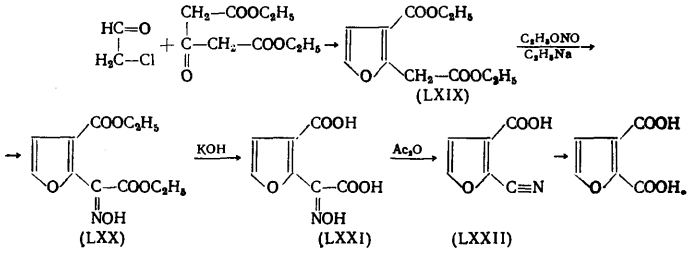
There exist several methods of synthesis for 2-methylfuran-3-carboxylic acid. The method of Plancher and Albini [189] is inconvenient, since the interaction of chloroethylideneacetoacetic ester with alcoholic ammonia was carried out in a sealed tube; the authors did not state the yield:



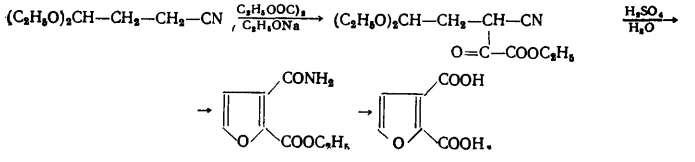
Benary [18] obtained the ester of this acid as an admixture with the ethyl ester of 2-methylpyrrole-3-carboxylic acid by the reaction of chloroacetaldehyde with acetoacetic ester in an ammoniacal medium. Gilman, who repeated the study [89], notes that the yield of 2-methylfuran-3-carboxylic acid is 40%.

There is also mention [69,96] of other methods of synthesis of the acid. As a rule, they consist of many stages and

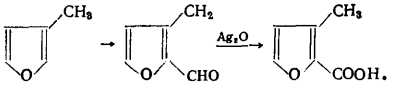
reduce to the decarboxylation of 5-methylfuran-2,4-dicarboxylic acid. Reichstein [132] also used the Benary method to prepare furan-2,3-dicarboxylic acid. He synthesised in 18% yield the ethyl ester of 3-ethoxycarbonylfuran-2-acetic acid (LXIX) by the condensation of chloroacetaldehyde with the diethyl ester of acetonedicarboxylic acid in the presence of ammonium hydroxide. Further reactions of the ester (LXIX) reduced to the synthesis of the oxime (LXX) and its subsequent conversion via compound (LXXI) and the nitrile (LXXII) into furan-2,3-dicarboxylic acid:



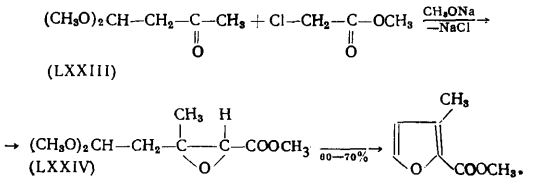
Later furan-2,3-dicarboxylic acid was obtained [170] from 4,4-diethoxybutyronitrile [190]:



As already mentioned above, 3-methylfuran-2-carboxylic acid was obtained for the first time from the natural ketone (LXVIII). Reichstein synthesised this acid from 3-methylfuran [90]:



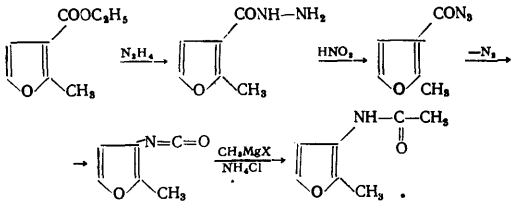
In 1956 Burness [131,138] proposed a new synthesis for 3-methylfuran-2-carboxylic acid whereby the latter became quite readily available. In this procedure the starting compound is the dimethyl acetal of formylacetone (LXXIII), which is converted quantitatively by the Darzens method, by the reaction with methyl monochloroacetate, into the glycidic ester (LXXIV), the distillation of which at 160°C leads to the methyl ester of 3-methylfuran-2-carboxylic acid:



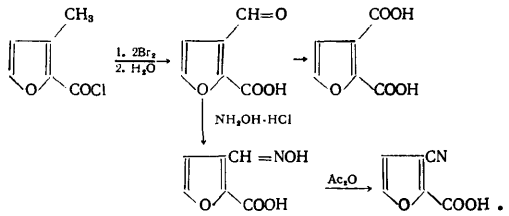
3-Phenylfuran-2-carboxylic acid was obtained similarly [138].

3. Reactions of 2-Methylfuran-3-carboxylic and 3-Methylfuran-2-carboxylic Acids

Although 2-methylfuran-3-carboxylic acid is essentially rather difficult to obtain, certain important studies have been carried out on its basis. Here we shall mention the synthesis [153] of 3-acetamido-2-methylfuran:

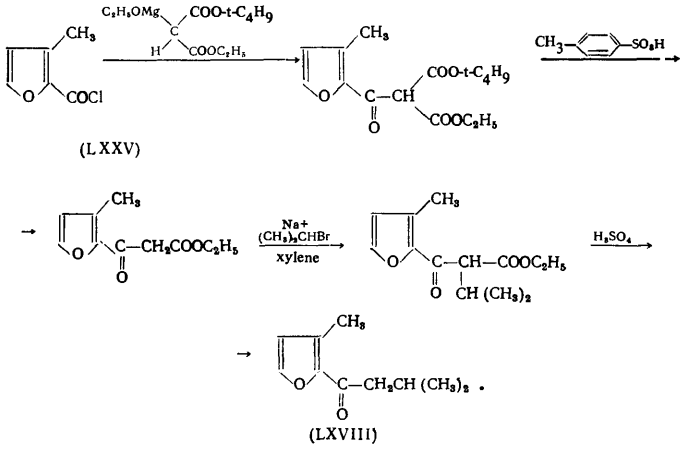


The isomeric 3-methylfuran-2-carboxylic acid has been much more widely used as a starting material for a wide variety of reactions. Asahina and Murayama [137], who obtained 3-methylfuran-2-carboxylic acid for the first time, synthesised from it certain 2,3-disubstituted furans. By the reaction of two moles of bromine with the chloride of this acid in direct sunlight at 130°C and subsequent hydrolysis, they obtained 3-formylfuran-2-carboxylic acid. On oxidation with silver oxide, the latter yielded furan-2,3-dicarboxylic acid:



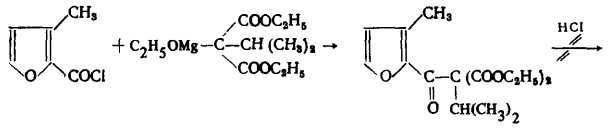
3-Cyanofuran-2-carboxylic acid was synthesised from the aldehydo-acid via the oxime.

In recent years there has been a considerable increase of interest in 3-methylfuran-2-carboxylic acid as a starting material. Ketones detected in natural products have been prepared from it. In 1963 Finan and Forthergill [191] synthesised the "Elsholtzia ketone" (LXVIII) in 50% yield using the acid chloride (LXXV) as the starting material:

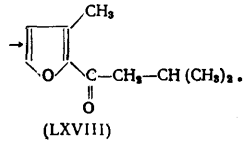


The attempts [191] to modify somewhat this synthesis in connection with data [192] concerning a new method for the preparation of the "perilla ketone" proved to be fruitless. Following the procedure of the Japanese investigators but using the acid chloride (LXXV) instead of the chloride of furan-3-carboxylic acid, Finan and Fothergill [191] condensed the acid chloride with the ethoxymagnesium derivative of

the diethyl ester of α-isopropylmalonic acid, but the ester (LXXVI) could not be cleaved to yield the ketone (LXVIII):

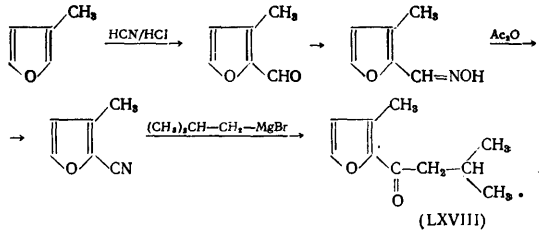


(LXXV) (LXXVI)



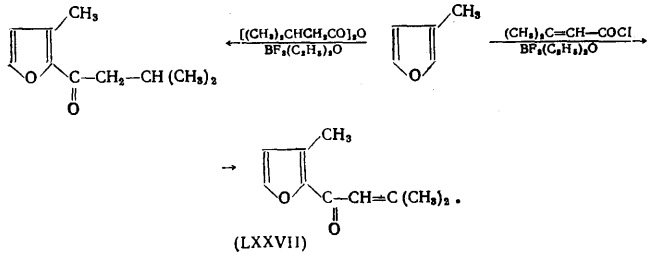
(LXVIII)

This finding is consistent with the observations of some workers [193,194], who showed that on treatment with an acid the diethyl esters of alkylated α-acylmalonic acid are not split with the formation of ketones. The structure of the "Elsholtzia ketone" (LXVIII) was confirmed for the first time in 1931 by Reichstein, who obtained it from 3-methylfuran in a low yield by the following procedure [90]:



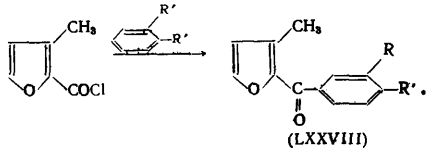
(LXVIII)

We may also mention here the formation of this ketone [173] in 30% yield when 3-methylfuran, which has become quite readily available, is acted upon by the anhydride of isovaleric acid. Some of its homologues have been synthesised similarly. The same workers obtained the "naginata ketone" (LXXVII) in 40% yield [195]:



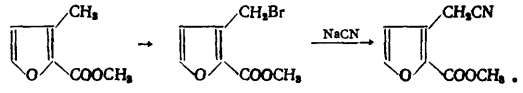
(LXXVII)

Leditschke [196] synthesised the hitherto unknown aryl 3-methylfur-2-yl ketones (LXXVIII) by the acylation of aromatic hydrocarbons with the chloride of 3-methylfuran-2-carboxylic acid:



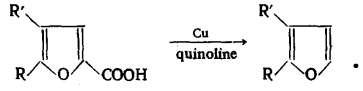
(LXXVIII)

Fairly recently the methyl ester of 3-bromomethylfuran-2-carboxylic acid was obtained [197] in a satisfactory yield by the reaction of *N*-bromosuccinimide with the methyl ester of 3-methylfuran-2-carboxylic acid in the presence of a radical-reaction initiator:

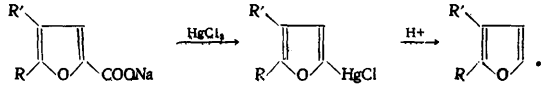


4. Elimination of One Substituent from Trisubstituted Furan Derivatives

The syntheses of 2,3-disubstituted furans from trisubstituted derivatives reduce to the reductive elimination of a halogen atom from certain trisubstituted furans [73,89] and decarboxylation [65,67,69,79,80,88,89,96,134,198–200] of the corresponding furan-2-carboxylic acid:



In the decarboxylation the authors [134] employed a method involving the intermediate replacement of the carboxy-group by a chloromercuri-group, which was subseqently eliminated by treatment with acid:



5. Substitution Reactions of Certain β-Monosubstituted Furan Derivatives

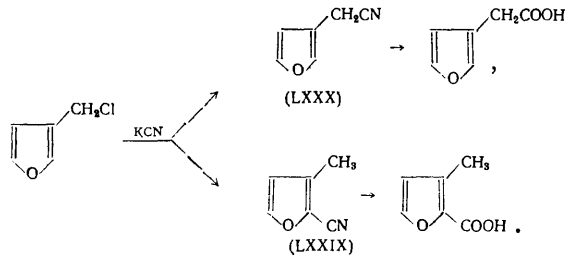
Until Gilman formulated the directing rule for mono-β-substituted furans in reactions involving the introduction of an electrophilic substituent into the ring [134,201], there existed only one example of reactions of this kind: the formylation [90] of 3-methylfuran by the Gattermann–Koch method. Having somewhat extended the number of mono-β-substituted furan derivatives, Gilman showed [134] that, when the existing β-group is *ortho*, *para*-directing in the benzene series, the new substitutent is directed to the adjacent α-carbon atom, forming 2,3-disubstituted furan; on the other hand, if the β-group is *meta*-directing, the new group forms a 2,4-disubstituted furan.

Gilman achieved the nitration of 3-methylfuran [134] and the chloromercuration of 3-methylfuran [201] and 3-isopropylfuran [79] with formation of the corresponding 2,3-disubstituted furans.

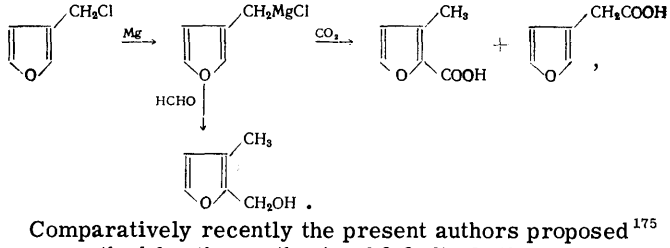
In view of the ready availability of 3-methylfuran, recently electrophilic substitution reactions with this compound have been carried out again, namely acylation [173] and bromination [197]. When 3-methylfuran was brominated with one mole of *N*-bromosuccinimide without a radical-reaction initiator, 2-bromo-3-methylfuran was obtained. When the amount of the brominating agent was varied, then, depending on the presence or absence of a radical-reaction initiator, various bromination products were obtained: with bromine either in the α-position of the furan ring or in the methyl group.

Sherman and Amstutz [202] made an interesting observation, namely that 2,3-disubstituted furan is formed as a result of the allyl rearrangement of certain β-monosubstituted furans of 3-chloromethylfuran under the action of

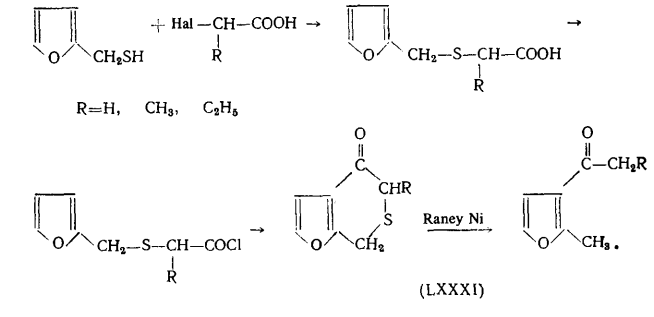
an aqueous solution of potassium cyanide and of fur-3-yl-methylmagnesium chloride under the action of carbon dioxide and formaldehyde. In the first case the product of the allyl rearrangement—3-methyl-2-furonitrile (LXXIX) —is formed only as an impurity in the main product fur-3-ylacetonitrile (LXXX):



In the second case the main product is 3-methylfuran-2-carboxylic acid (90% yield) or 3-methylfurfuryl alcohol (33% yield) is obtained as the sole product:



Comparatively recently the present authors proposed[175] a new method for the synthesis of 2,3-disubstituted furans —allyl 2-methylfur-3-yl ketones. It consists in the formation from the readily available 2-substituted furans of bicyclic condensed systems with a "bridge" between the second and third positions in the furan ring incorporating a sulphur atom in one of the units. This unit, separated from the ring by carbon atoms, is eliminated in the next stage by Raney nickel. The elimination of sulphite sulphur from the side chain by Raney nickel takes place without appreciable reduction of the furan ring to the tetrahydrofuran derivative:



In the course of the synthesis of 2,3-disubstituted furans a new condensed bicyclic compound (LXXXI) was obtained and some of its properties were investigated.

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Zelinskii Institute of Organic
Chemistry, Moscow

U.D.C. 547.74/.73

N-Vinyl Compounds of the Pyrrole Series

M.F.Shostakovskii, G.G.Skvortsova, and E.S.Domnina

The review deals with the methods of synthesis and reactivities of *N*-vinyl derivatives of pyrrole, indole, and carbazole. Their chemical properties have been compared with one another and also with those of aryl vinyl ethers and enamines. Since the reactions of *N*-vinyl pyrroles have been inadequately investigated, all the principal chemical properties of this series will be considered—mainly with *N*-vinylindole as an example, this compound having been most thoroughly investigated by the authors of the review. The bibliography includes 201 references.

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I. INTRODUCTION

Heterocyclic compounds containing a nitrogen atom in the ring are extremely widely distributed in nature as alkaloids, vitamins, and pigments, and play a very important role in biological processes [1,2]. Many compounds with an indole ring exhibit high pharmacological activity [3].

In recent years unsaturated *N*-heterocyclic compounds have been attracting attention because of their high and unusual reactivity. The vinyl derivatives of pyrrolidone and various other lactams are already used in the plastic and synthetic fibres industry, electronic engineering, and medicine and have been frequently described [4,5]. Among the *N*-vinyl compounds, *N*-vinylindole remained completely uninvestigated for a long time. The introduction into the indole molecule of a vinyl group conjugated via the nitrogen atom with the π-electrons of the double bonds of the benzopyrrole system opens up a path to the synthesis of more complex compounds, including macromolecular compounds. This gives rise to great potential possibilities for the synthesis of new antimicrobial and medicinal preparations, organic semiconductors, and thermally and electrically insulating coatings.

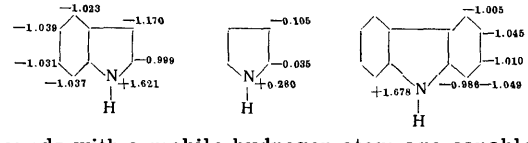
The information in the literature about the chemistry of the parent compound of this series, *N*-vinylpyrrole, is very limited. Only the problem of the preparation and polymerisation of *N*-vinylcarbazole is discussed. Furthermore, the available published data on the *N*-vinyl compounds of pyrrole and its benzo-derivatives have not so far been compiled.

II. METHODS OF SYNTHESIS OF *N*-VINYLPYRROLES

Vinyl derivatives of nitrogen-containing heterocycles may be synthesised in different ways. The methods for their preparation can be divided into several groups in accordance with the reaction on which their synthesis is based: (1) direct vinylation; (2) dehydration of β-hydroxyethyl derivatives of heterocycles; (3) dehydrohalogenation of halogenoethyl derivatives of heterocycles.

1. Direct Vinylation

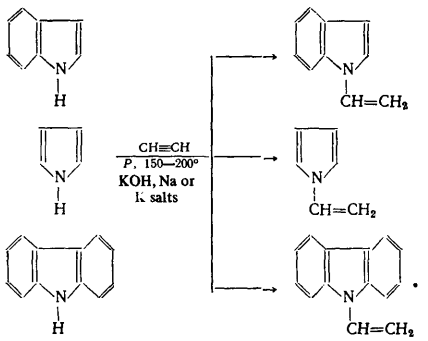
As a result of π-electron conjugation, the electron density at the nitrogen atom in pyrrole, indole, and carbazole molecules is transferred to the ring, which leads to considerable polarisation of the N–H bond. This effect may be regarded as the main reason for the enhanced mobility of the hydrogen atom attached to the nitrogen atom. Recent theoretical calculations confirmed the presence of an excess positive charge at the nitrogen atom of pyrrole systems [1,6]:



Compounds with a mobile hydrogen atom are capable of interacting with acetylene to form vinyl derivatives [7]. The vinylation reaction is based on the work of Favorskii [8], who showed that alcohols add to substituted acetylenes with formation of vinyl ethers. Shostakovskii [9], Prilezhaeva [10], Kalabina [11], and Sidel'kovskaya [12,13] extended this reaction to mercaptans, phenols, lactams, and thiono-amides. Foreign studies in this field have been carried out by German chemists led by Reppe [14,15] and a number of American [16,17] and Japanese [18,19] scientists.

The available literature data show that the vinylation of amino-compounds is more complex than that of alcohols, phenols, and mercaptans. Recently Chekulaeva [20] reviewed the information about the reactions of acetylene with amines and ammonia and described the principal laws governing these reactions. Primary and secondary aliphatic amines react with acetylene in the presence of alkalis, forming resins [14]. The replacement of alkali by zinc or cadmium salts leads to the synthesis of unstable vinylamines [15,20]. Stable products are obtained when heterocyclic imino-compounds are vinylated. The methods of their preparation have been described systematically in individual sections of review articles [14–16,21–23] and also in monographs [5,24].

Usually the interaction of compounds of the pyrrole series with acetylene takes place at elevated temperatures and a pressure of 15–20 atm in the presence of basic catalysts. The latter are alkali metal salts of the compounds vinylated and also substances which are capable of substituting by an alkali metal the hydrogen of the imino-group in the pyrrole molecule:



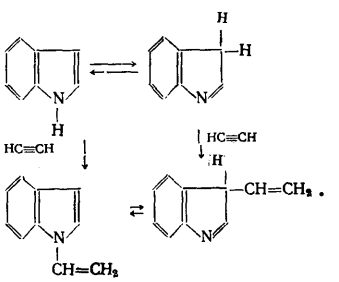
Sodium and potassium hydroxides or alkoxides are frequently employed [15,25] and alkali metals less so [26]. The catalyst is also treated with promoting agents, which make it possible to carry out the reaction at lower pressures and temperatures, accelerate the main vinylation process, and increase the yield. Agents of this kind which have been employed are zinc oxides [27,28], powdered zinc [29,30], and zinc carbonate, phosphate, and sulphide [31]. Sometimes small amounts of ammonia, pyridine, or quinoline are added to the reaction mixture in order to accelerate the reaction [31,32]. The catalyst usually consists of three parts of potassium hydroxide and one part of zinc oxide and is added in an amount of 3–4%. The reaction is normally performed in solution or in suspension. It is very important to carry out the process in an organic solvent which dissolves the vinylated compound, for example benzene, toluene, cyclohexane, methylcyclohexane, decalin, and dimethylcyclohexanol [33]. Acetylene is diluted with nitrogen, carbon dioxide, or methane in proportions of 2 : 1. The reaction lasts 4–5 h. Carbazole is also vinylated at 180°C in the presence of sodamide and calcium carbide in ligroin [34]. *N*-vinylcarbazole is synthesised in high yields at 200°C in ethyl vinyl ether solution [35].

In the reaction of an equimolar mixture of technical fluorine and carbazole with acetylene at a pressure of 39 atm and 195°C in toluene in the presence of potassium hydroxide and added quinoline, Karpukhin and Levchenko [36,37] obtained in 61% yield a mixture of vinyl derivatives containing 45% of *N*-vinylcarbazole.

Pyrrole and its benzo-derivative are also vinylated in the gas phase at atmospheric pressure and a temperature of 250–320°C, but the yield of products is much lower than in the vinylation in the aqueous phase [38,39]. Pyrrole vapour has been vinylated with acetylene over the Fe/K_2CO_3 catalyst at 300°C and a pressure of 300–500 mm. [15] In 1962 a new method was proposed for the synthesis of *N*-vinylpyrrole [40] by allowing gaseous acetylene and pyrrole to come into contact at 150–350°C with a catalyst consisting of an MgO carrier impregnated with 5–15% KOH.

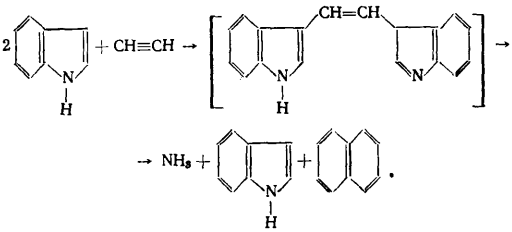
The information about the synthesis of *N*-vinylindole is very limited. Indirect indications of the possibility of the preparation of *N*-vinylindole by analogy with *N*-vinylcarbazole and *N*-vinylpyrrole appeared for the first time in the 1930's in a number of patents [29,28,41]. Reppe [27] describes the synthesis of *N*-vinylindole by the reaction of indole with acetylene under pressure in the presence of 2% KOH at 150–160°C for 70 h. In the 1950's Kawasaki [42] noted that an increase in the amount of KOH and of temperature to 180°C and the use of a potassium salt of indole instead of potassium hydroxide reduces the duration of heating to 4–5 h. *N*-Vinylindole was also synthesised by passing a mixture of indole and acetylene vapours over an iron catalyst at 300°C. [15]

Shostakovskii et al. [43], who studied the vinylation of indole, showed that this is a complex process, since under the conditions of this reaction not only indole itself but also its tautomeric form—pseudoindole—can exist. Nowadays it is no longer surprising that indole and pyrrole are protonated both at nitrogen and carbon. This is indicated by preliminary data obtained in the study of the ionisation of these compounds [44]. One cannot exclude the possibility that both tautomeric forms of indole, which have active hydrogen atoms in positions 1 and 3, can react with acetylene to form *N*-vinylindole and pseudovinylindole by the mechanism



The latter is probably formed as a result of the migration of the vinyl group in the *N*-vinylindole molecule under the conditions of the reaction.

Shostakovskii et al. [43] assumed that the high-boiling compound which they isolated is formed as a result of the interaction of both tautomeric forms of indole with an acetylene molecule. On heating it decomposes into ammonia, indole, and naphthalene:

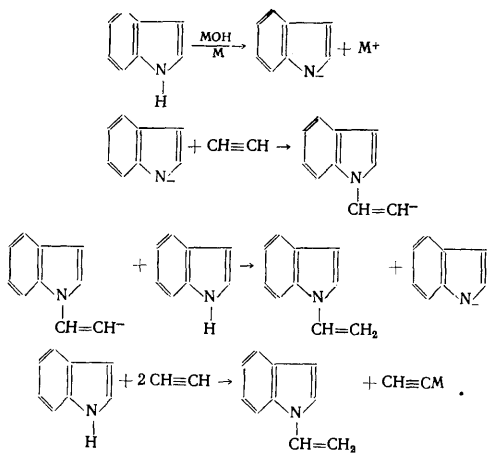


Later Domnina, Skvortsova, and coworkers investigated the reaction of indole with acetylene under pressure in order to drive the reaction towards the optimum degree of formation of one of the tautomeric forms—*N*-vinylindole. They showed that the yield of the latter compound is significantly improved when the reaction is carried out in toluene or dioxan with small amounts of water (about 10%). The solvent favours the ionisation of the initial component and an increase of the concentration of acetylene in the reaction mixture. Potassium hydroxide (about 30%) and sodium hydroxide have been recommended as catalysts [45]. The variation of the yield of *N*-vinylindole with the concentration of potassium hydroxide, the amount of water, temperature, and the duration of the vinylation of indole has been investigated [46]. A decrease of the concentration of potassium hydroxide to 25% lowers the yield of *N*-vinylindole almost by a factor of two. Heating above 220°C leads to thermal polymerisation of the vinylation product. The best result, with the yield of *N*-vinylindole reaching 90% of theoretical, was achieved when indole was allowed

to react with acetylene at 180°C in the presence of 5.5% of metallic potassium [47]. The process takes 30 min. An increase of the duration of the reaction leads to enhanced tar formation.

When the potassium salt of indole is used as a catalyst, the vinylation takes place under the same conditions, the yield of *N*-vinylation reaching up to 88%. The replacement of potassium hydroxide by metals (sodium, lithium, and their salts) proved to be less effective, since the process had to be carried out at a higher temperature (up to 220°C), which results in the polymerisation of the *N*-vinylindole formed.

By analogy with other cyclic imines [48], the mechanism of the vinylation of indole can be represented as follows:



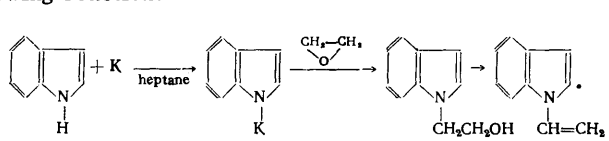
This is confirmed by the synthesis of *N*-vinylindole from potassium indolate when the latter reacts directly with acetylene.

The method of synthesis of *N*-vinyl derivatives of the pyrrole series by direct vinylation has many advantages: the process consists of a single stage, the yields are high, and in many cases the starting material is readily available. However, experiments at elevated pressures and temperatures are complicated by the risk of explosion of acetylene. Therefore in many countries other methods for the introduction of the vinyl group into heterocyclic compounds are being developed together with studies designed to widen the scope of the syntheses based on acetylene, and these are considered below.

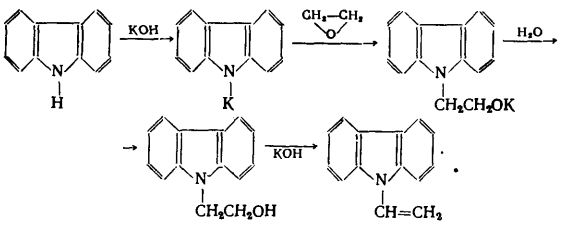
2. Dehydration of β-Hydroxyethyl Derivatives of Heterocyclic Compounds

Carbazole derivatives are dehydrated at a reduced pressure and an elevated temperature, frequently in the presence of potassium hydroxide. In a few cases acid catalysts are employed (potassium hydrogen sulphate, sulphuric acid, acetic anhydride, or alumina).

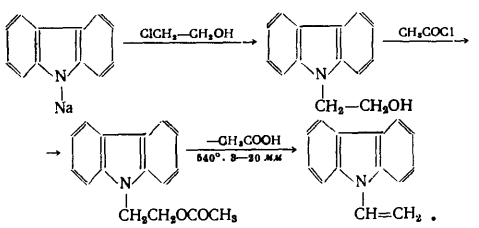
Japanese investigators [49] synthesised *N*-vinylindole from potassium indolate and epoxyethane in 40.5% yield by the following reaction:



They obtained *N*-vinylpyrrole similarly in 23.6% yield. Other workers [50–52] synthesised *N*-vinylcarbazole by the dehydration of *N*-(β-hydroxyethyl)carbazole using the reaction



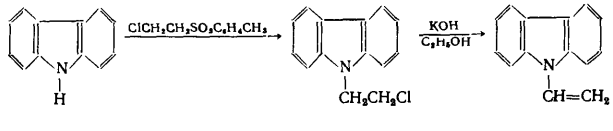
Sometimes the sodium salt of carbazole is used instead of the potassium salt [50,53]. The hydroxy-derivative obtained from the salt and ethylenechlorohydrin is treated with an excess of acetic acid, acetyl chloride, or acetic anhydride and then pyrolysis of the resulting acetate yields *N*-vinylcarbazole:



Lopatinskii et al. [54] obtained *N*-vinylcarbazole in 70–75% yield by the dehydration of *N*-(β-hydroxyethyl)carbazole with 10% potassium hydroxide at 250–270°C. In order to obtain β-hydroxyethyl derivatives, they also used the interaction of halogenocarbazoles with epoxyethane [55,56]. In a recently proposed method [57] *N*-vinylcarbazole and its 3-chloro- and nitro-derivatives are synthesised by the vacuum pyrolysis of the corresponding *N*-(α-acetoxyethyl)-carbazoles, which are readily obtained by the addition of vinyl acetate to carbazoles in solution in aliphatic ketones in the cold in the presence of solid alkalis [58]. The process can be carried out in a single stage without the isolation of the intermediates. The yields of *N*-vinylcarbazoles reach 65–80% of theoretical [59]. In its efficiency the method surpasses all other known methods for the preparation of 3-chloro-*N*-vinylcarbazoles.

3. Dehydrohalogenation of Halogenoethyl Derivatives of Heterocyclic Compounds

The elimination of hydrogen halides from the corresponding α- and β-halogenoethyl derivatives of nitrogen-containing heterocycles is achieved by the action of bases (potassium hydroxide, sodium ethoxide and methoxide, pyridine, sodamide, trimethylamine). Clemo and Perkin [60] obtained *N*-vinylcarbazole and *N*-vinyl-1,2,3,4-tetrahydrocarbazole by the elimination of hydrogen chloride from *N*-(β-chloroethyl)carbazole with alcoholic alkali at 50–60°C:



N-(β-chloroethyl)carbazole is synthesised by the reaction of β-chloroethyl *p*-toluenesulphonate with carbazole in acetone solution in the presence of alkali.

Lopatinskii and Zherebtsov[61] discovered the conditions for the conversion of 3-chloro-, 3,6-dichloro-, 3-bromo-, and 3,6-dibromo-carbazoles into the corresponding *N*-vinyl derivatives. Initially they substituted the hydroxyl in 3-chloro-*N*-(β-hydroxyethyl)carbazole by chlorine using phosphorus pentachloride and then dehydrochlorinated the product by the method described above[60].

Certain other procedures are also used to synthesise *N*-vinyl heterocyclic derivatives. Thus it has been stated that *N*-vinyl derivatives are formed when indole and carbazole react with vinyl acetate in solution in aliphatic ketones in the presence of mercury sulphate and sulphuric acid[62,63]. Unfortunately, however, the resulting vinyl compounds are polymerised under the reaction conditions.

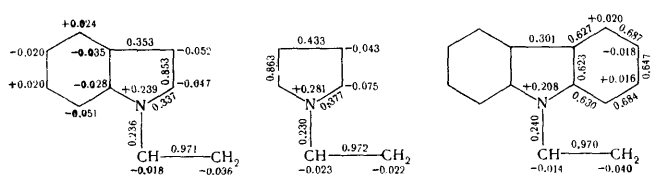
The introduction of a vinyl group into the carbazole molecule by the reaction of the potassium salt of carbazole with vinyl chloride in dimethylcyclohexane under pressure was described as early as the 1930's.[15,64,65]

III. CHEMICAL PROPERTIES OF *N*-VINYLPYRROLES

Although the molecules of *N*-vinyl derivatives of pyrroles and benzopyrroles contain many reaction centres, the chemistry of these compounds has so far been little investigated. For a long time attention was concentrated in the literature solely on the study of the polymerisation of *N*-vinylcarbazole, whereby it is possible to obtain products with valuable properties.

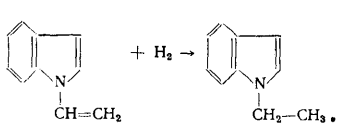
1. Addition Reactions at the Double Bond of *N*-vinylpyrroles

Quantum-mechanical calculations using the semi-empirical self-consistent field MO-LCAO method by Frolov and Kontarev[66,67] showed the following distribution of electron density in the molecules of vinyl derivatives of pyrrole, indole, and carbazole:



The molecular diagrams indicate an increase in the π-electron density at the β-carbon atom of the vinyl group and also at the C_2–C_3 bond of the pyrrole ring. According to modern theoretical concepts, the addition of electrophilic agents to the β-carbon atom of the vinyl group is due to the positive mesomeric and electromeric effects of the imino-nitrogen.

Addition of hydrogen. In the presence of Raney nickel in an alcoholic medium at room temperature and atmospheric pressure *N*-vinylindole readily adds hydrogen to the double bond of the vinyl group, forming *N*-ethylindole[46], the yield of which reaches 80–90%:



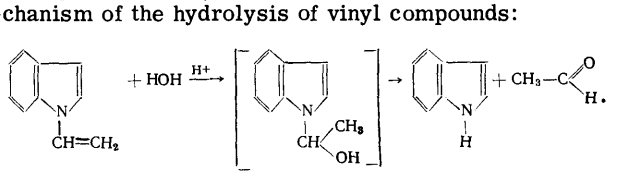
Kawasaki[42] hydrogenated *N*-vinylindole in the presence of the palladium/charcoal catalyst.

N-vinylcarbazole is also readily hydrogenated to *N*-ethylcarbazole[16]. Reppe[15] carried out this process in methanol in the presence of Raney nickel at 80°C and a hydrogen pressure of 15 atm.

Hydrolysis. Like *N*-vinyl-lactams[68], *N*-vinylimides[69,70], and vinylethers[71], *N*-vinylpyrroles are split by mineral acids at the C–N bond with formation of acetaldehyde and pyrroles. Comparison of the literature data[68–71] shows that the hydrolysis of *N*-vinylcarbazole is more difficult than that of *N*-vinyl-lactams and vinyl ethers. The hydrolysis of *N*-vinylcarbazoles requires longer heating and a higher concentration of catalysts. Furthermore, the process is accompanied by side reactions which made it impossible for a long time to isolate the acetaldehyde produced in the reaction, since it immediately interacts with the carbazole to give a crystalline product of unknown structure[60]. When hydrazine hydrate is added to the initial reaction mixture, the hydrolysis goes to completion and acetaldehyde hydrazone is formed almost quantitatively[5]

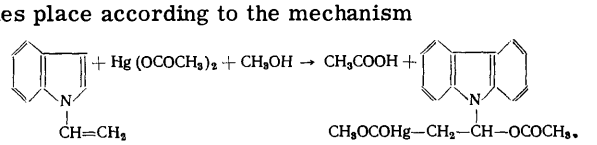
By hydrolysing *N*-vinylcarbazole for four days in a 9 : 1 mixture of methanol and water in the presence of iron(III) nitrate, it proved possible to isolate[72] carbazole and acetaldehyde, identified as the 2,4-dinitrophenylhydrazone. The reaction is accompanied by the formation of 20% of *trans*-1,2-dicarbazolylcyclobutane; the mechanism of this process has been discussed[72].

Shostakovskii et al.[73] investigated the acid hydrolysis of *N*-vinylindole. By varying the concentration of sulphuric acid, temperature, and the duration of reaction, they found that *N*-vinylindole is hydrolysed most completely (to the extent of 97–98%) after 30 h at 60°C in the presence of 4% H_2SO_4. In the presence of a more dilute acid (0.5–3%) the degree of hydrolysis at 30°C did not exceed 15–16%. Shostakovskii et al.[73] suggest that the hydrolysis of *N*-vinylindole proceeds according to the following mechanism, which is analogous to the general mechanism of the hydrolysis of vinyl compounds:



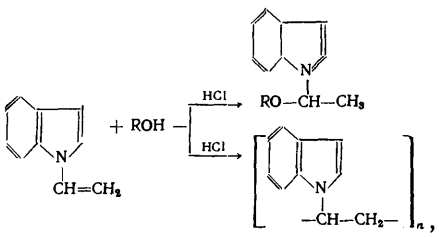
In contrast to *N*-vinylcarbazole, in this case the formation of by-products was not observed; *N*-vinylindole is much more difficult to hydrolyse than alkyl vinyl ethers and *N*-vinyl-lactams[7,74]. However, it is hydrolysed at a lower temperature than aryl vinyl ether. *N*-vinylindole is stable when heated for a long time in dilute alkalis.

Addition of alcohols. Of the reactions involving addition to *N*-vinylcarbazole by a polar mechanism, the interaction of this compound with mercury acetate, which is used for the analytical determination of the monomer, has been described[75]. In absolute methanol the addition takes place according to the mechanism



Skvortsova et al.[76] showed that two competing reactions occur in the interaction of *N*-vinylindole with aliphatic alcohols, phenols, and monocarboxylic acids. The addition of an alcohol to the vinyl group of *N*-vinylindole is accompanied by its homopolymerisation. The alcohols

add in accordance with the Markovnikov rule and the results of quantum-mechanical calculations:

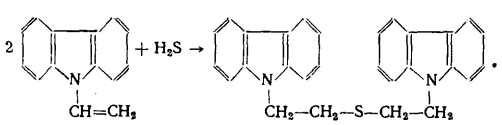


where R = CH_3, C_2H_5, C_3H_7, C_4H_9, or C_6H_5.

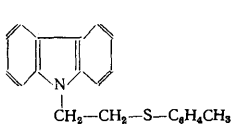
Depending on the reaction temperature, the order of addition of the components, and the nature of the hydroxy-compound, one or other process predominates. It has been established that methanol, ethanol, and propanol react with *N*-vinylindole at temperatures ranging from −7° to +5°C with formation of *N*-α-(methoxy-, ethoxy-, propoxy-)-ethylindoles, their yields reaching 66–74%. C_4 and higher alcohols and also phenols do not add to *N*-vinylindole, since under the reaction conditions (18–20°C) the polymerisation of this compound predominates. It proved impossible to acylate *N*-vinylindole at the double bond of the vinyl group by acids such as formic, acetic, butyric, isobutyric, and valeric. Depending on the strength of the initial acid, *N*-vinylindole polymerises instantly or after several hours.

Addition of thiols. Shostakovskii et al.[77-80] made a detailed study of the thiolation of alkyl vinyl and aryl vinyl ethers and *N*-vinyl-lactams. In her review Prilezhaeva[81] states that the addition of hydrogen sulphide and mercaptans to αβ-unsaturated compounds in the presence of free radical initiators is accompanied by the formation of β-addition products.

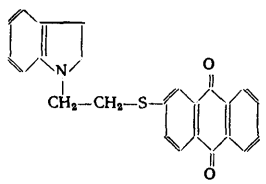
The addition of hydrogen sulphide to *N*-vinylpyrroles is also contrary to the Markovnikov rule[15,16]. Reppe and Nikolai[82,83] obtained di-β-(*N*-carbazolyl)ethyl sulphide by passing hydrogen sulphide into an alcoholic solution of *N*-vinylcarbazole heated to 75°C and containing a small amount of potassium hydroxide:



They synthesised di-β-(1-indolyl)ethyl sulphide by the action of hydrogen sulphide at 80°C on a solution of *N*-vinylindole in butanol in the presence of metallic potassium in an amount of about 0.1%. The reaction of *N*-vinylcarbazole with methane-, ethane-, butane-, dodecane-, and toluene-thiols, thiophenol, thiocresol, chlorothioxylene, thionaphthol, 1- or 2-mercaptoanthraquinone, thioresorcinol, and mercaptobenzothiazole is anomalous[82]. Thus, when thiocresol is refluxed with *N*-vinylcarbazole in a fairly dilute alcoholic solution for 12 h, β-(*N*-carbazolyl)ethylthio-*p*-toluene is formed in the absence of a catalyst:

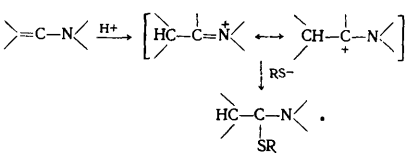


2-Mercaptoanthraquinone reacts with *N*-vinylcarbazole to form 2-anthraquinonylthio-1-(*N*-carbazyl)ethane:

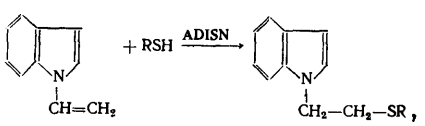


The possibility of an analogous interaction of *N*-vinylpyrrole with hydrogen sulphide and mercaptans to form β-addition products is indicated in patents[82,83], but concrete examples with description of reaction conditions are not given.

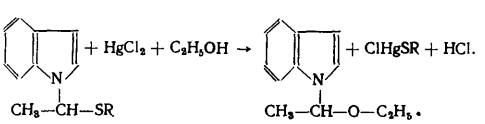
Investigations in recent years showed that certain *N*-vinyl compounds combine with mercaptans in accordance with the Markovnikov rule even under the influence of radical initiators (as in their absence). Leonard and Hay[84] and Lawesson and coworkers[85] found that cyclic enamines interact with mercaptans, forming α-addition products:



Shostakovskii et al.[86] developed a method for the preparation of new sulphur compounds of the indole series consisting in the interaction of *N*-vinylindole with mercaptans. They showed that free-radical addition of thiols to *N*-vinylindole under the influence of azodi(isobutyronitrile) (ADISN) takes place mainly with formation of *N*-(β-alkylthioethyl)indole (yield 75–80% of theoretical):

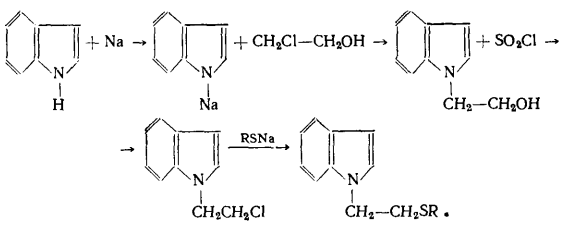


where R = H, C_2H_5, iso-C_3H_7, or t-C_4H_9. Together with this compound, a mixture of α- and β-addition products was isolated. The structure of *N*-(β-ethylthioethyl)indole was demonstrated unambiguously by proton magnetic resonance. Its spectrum consists of four multiplets comprising three triplets (δ = 1.0, 2.57, and 3.96 p.p.m.) and a quartet (δ = 2.14 p.p.m.). The presence of α-addition products is confirmed by the reaction with an alcoholic solution of mercuric chloride[78,87,88]:



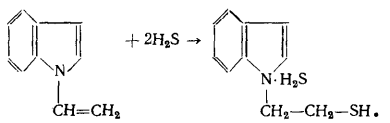
The amount of acid produced from the various alkylthio-derivatives varies from 38 to 95%. The physical constants of *N*-(α-ethoxyethyl)indole isolated from the reaction mixture agree with those of the products of the addition of ethanol to *N*-vinylindole[89,90].

To confirm the structure of the alkylthio-derivatives of *N*-vinylindoles, Domnina [89] attempted an indirect synthesis of the β-addition products by the following process:



Owing to the great tendency of indole derivatives to undergo dimerisation and polymerisation in an acid medium, this synthesis could not be taken to completion [91].

On heating to 80°C in the absence of an initiator, mercaptans do not add to *N*-vinylindole and, when the reaction mixture is distilled, the starting materials are completely recovered. Acidic catalysts, such as sulphur dioxide or *p*-toluenesulphonic acid, also do not facilitate their interaction and at different reaction temperatures only *N*-vinylindole pentamers and hexamers are produced [90]. According to a patent application [82], a sulphide derivative could not be isolated in the reaction of *N*-vinylindole with hydrogen sulphide. It was established that at 80°C *N*-vinylindole interacts with two hydrogen sulphide molecules:

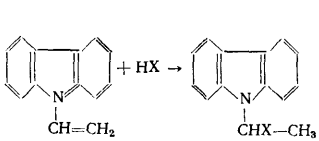


The present authors believe that, by analogy with mercaptans the HS group adds to the β-carbon atom of the vinyl group and the second hydrogen sulphide molecule forms a salt [89].

Halogenation and hydrohalogenation reactions. Studies on the halogenation of *N*-vinyl compounds are limited to only a few examples. The interaction of *N*-vinylcarbazole with bromine is mentioned in Reppe's review [15]. Reppe believes that, in the presence of potassium carbonate at −10°C, *N*-vinylcarbazole reacts with bromine to form methoxybromoethylcarbazole. The structure of the product was not proved. According to a patent [92], *N*-vinylcarbazole polymerises under the action of a small amount of hydrogen chloride.

Pielichowski and coworkers [93,94] recently described the halogenation and hydrohalogenation of *N*-vinylcarbazole. They suggest that bromination with a solution of bromate and bromide involves the vinyl group with formation of a product containing three or six bromine atoms, i.e., together with the addition reaction, hydrogen atoms are also substituted by bromine.

Pielichowski [94] believes that the addition of hydrogen halides to *N*-vinylcarbazole takes place in accordance with the Markovnikov rule, α-halogenoethylcarbazoles being formed:

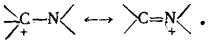


The reaction is carried out in carbon tetrachloride solution, through which hydrogen chloride, bromide, iodide, or fluoride is passed during 1 h. The addition products have the following melting points respectively: 255°, 165°, 165–166°, and 123–125°C. The structure of the chloro-derivatives is confirmed by the fact that they differ in their properties from those of *N*-(β-chloroethyl)-carbazole synthesised earlier by Clemo and Perkin [60].

For a long time there was no information in the literature about the halogenation of *N*-vinylindole. Shostakovskii et al. found that chlorine and bromine react vigorously with *N*-vinylindole in the cold in carbon tetrachloride. By analogy with the hydrogenation of vinyl ethers [7] and also *N*-vinylphthalimide [96] and in agreement with data obtained by elemental analysis, the authors initially suggested that bromine adds to *N*-vinylindole at the vinyl group with formation of *N*-(αβ-dibromoethyl)indole or tribromoethylindole. However, subsequent studies of the halogenation of *N*-vinylindole established that, depending on the relative amounts of the starting components and the duration of interaction, polymeric products with various halogen contents are obtained [66] (for a more detailed description, see p. 415).

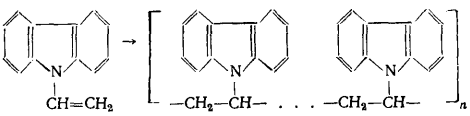
2. Polymerisation

The structure of the group linked to the nitrogen atom strongly influences the activity of *N*-vinyl compounds in polymerisation. Aliphatic vinylamines are known to be inactive in polymerisation. Plesch [97] explains this inertness of the growing chain by the resonance



In vinylcarbazole this difficulty is overcome as a result of the tendency to retain the aromatic properties of the heterocyclic compound. Because of this, *N*-vinylcarbazole is capable of polymerisation on heating above its melting point (85°C) without catalyst [98,99]. *N*-vinylindole also polymerises readily [46].

Among the vinyl monomers of the pyrrole series, *N*-vinylcarbazole has been most thoroughly investigated [15,100–102]. It can be readily polymerised by the usual methods—in the solid state, in solution, in emulsion, and in suspension in the presence of various initiators [103,104]. The reaction leads to the formation of a linear polymer with the following structure:



N-Vinylcarbazole and *N*-vinylindole undergo both cationic and radical polymerisation and therefore differ from vinyl ethers, which polymerise exclusively under the action of acid reagents [7,105–107].

t-Butylperoxide, azodi(isobutyronitrile), and hydrogen peroxide are used as the radical initiators of the block polymerisation of *N*-vinylcarbazole [108–110]. Benzoyl peroxide does not initiate the polymerisation of *N*-vinyl compounds [111]. Alkaline oxidising agents [5], such as sodium peroxide, perborate, and dichromate are catalysts for the radical polymerisation of *N*-vinylcarbazole in suspension. In the presence of 0.005–0.01% of azodi(isobutyronitrile) *N*-vinylcarbazole is converted into an almost colourless high-molecular polymer [112], while in an aqueous dispersion grains 0.5–1 mm in diameter are produced [113]. Organic bases inhibit its polymerisation [114].

The cationic polymerisation of *N*-vinyl compounds of the pyrrole series takes place readily. Boron trifluoride, various metal chlorides such as zinc chloride, aluminium chloride, etc., acid chlorides (sulphuryl, thionyl, acetyl,

and benzoyl chlorides), and halogeno-hydrocarbons are widely used in this case [92,115-118].

The solid-phase polymerisation of *N*-vinylcarbazole in the presence of Friedel–Crafts catalysts yields polymers with a low molecular weight [119]. In liquid sulphur dioxide at temperatures between −10° and −70°C *N*-vinylcarbazole and *N*-vinylpyrrole form polymers with high molecular weights reaching 90 000. [116,117] The reaction takes place by an ionic mechanism with the initial formation of a complex of *N*-vinylcarbazole with sulphur dioxide [120,121]. These products have valuable technical properties, mainly as impregnating materials [122,124].

N-Vinylcarbazole polymerises even in the presence of morpholine [125]. In the search for the synthesis of pure high-molecular polyvinylcarbazole organic compounds such as *p*-chloroaniline [126], various pyrylium salts [127], and also methyl methacrylate (1–10%) have been investigated as initiators [128]. Recently Japanese workers [129] found that *N*-vinylcarbazole polymerises by a cationic mechanism in the presence of electron acceptors such as gaseous chlorine, sulphur dioxide, and maleic anhydride [130,131]. They suggest that the monomer forms with the acceptor a charge-transfer complex, which is a source of cationic radicals with a localised carbonium ion. Such complexes exhibit paramagnetic properties and initiate the polymerisation of *N*-vinylcarbazole.

When electron acceptors such as dichlorodicyanobenzoquinone, *p*-chloranil, dichlorobenzene, and others were employed [49], the polymerisation activity decreased in the series *N*-vinylcarbazole > *N*-vinylindole > *N*-vinylpyrrole.

The anionic-coordination polymerisation of *N*-vinylcarbazole is carried out in the presence of t-C_4H_9Li–$TiCl_4$ Ziegler–Natta catalysts [132]. The maximum yield of the isotactic polymer reaches 80% for the ratio Li : Ti = 1.5 : 1.7.

Polyvinylcarbazole was obtained in 23–100% yield at temperatures between −78° and +80°C when $C_2H_5AlCl_2$, $(C_2H_5)_2AlCl$, $TiCl_2(OC_3H_7)_2$, $FeCl_2(OCOCH_3)_2$, and $SnCl_2(OCOCH_3)_2$ were used as catalysts [133].

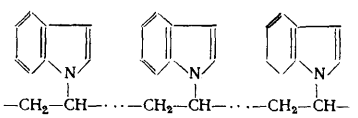
The solid-phase polymerisation of *N*-vinylcarbazole on irradiation with sunlight, ultraviolet light, and γ-rays has been investigated [134-137].

Although the methods for the polymerisation of *N*-vinylcarbazole using all the catalysts enumerated above have been described in many patents, the polymers obtained in this way have not found practical application due to their low molecular weight. The development of the *N*-vinylcarbazole industry in the USA showed that high-molecular weight polymers are mainly manufactured. They are distinguished by their stability to high temperatures and chemical reagents and also by low dielectric constants; such polymers are obtained only by alkaline oxidative polymerisation in emulsion [138]. The process is carried out under a pressure of about 18 atm at 120–180°C. Special initiating agents are potassium or sodium dichromate in an alkaline medium.

Polyvinylcarbazole resins are widely used as surface coatings, for the impregnation of paper, and for the protection of electrical equipment [2].

The information in the literature about the properties and methods of preparation of polyvinylindole is extremely limited. There exist several foreign patents [109,114,116] where the possibility of the polymerisation of *N*-vinylindole is indicated, by analogy with its homologue—*N*-vinylcarbazole. An *N*-vinylindole polymer with a high softening point was obtained by Kawasaki [42] at room temperature in the presence of 4% hydrogen chloride. Schildknecht [100] described the polymerisation of *N*-vinylindole under the influence of 0.01% $BF_3(OC_4H_9)$ below 25°C.

To elucidate the reactivity of the double bond of *N*-vinylindole in polymerisation reactions, Domnina and Skvortsova [139] studied this reaction under the influence of ionic catalysts and free radical initiators. The metal chlorides $SnCl_2.2H_2O$, $SnCl_4$, $AlCl_3$, $TiCl_4$, $TiCl_3$, $FeCl_3$, and also $BF_3O(C_2H_5)_2$ were tested as cationic catalysts. In the presence of 2% $SnCl_4.5H_2O$ *N*-vinylindole polymerises to the extent of 96–98% in 24 h. By analogy with the structural formula of polyvinylcarbazole, it is suggested that the principal unit in polyvinylindole may have the following structure:



The study of the molecular weight distribution in the polymerisation product of *N*-vinylindole by a fractionation procedure showed that polyvinylindole consists mainly of a weakly disperse mixture of polymeric homologues. The maximum on the differential distribution curve is located at low molecular weights, between 700 and 1000, and is fairly broad.

The calculated viscometric constants in the Mark–Houwink equation indicate an extended, rigid, rodlike structure of the polyvinyl molecule and suggest that the latter exhibits electrolytic properties.

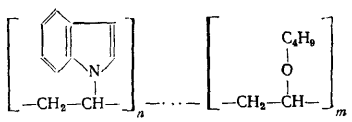
In the presence of benzoyl peroxide *N*-vinylindole does not polymerise, while hydrogen peroxide gives rise to its quantitative conversion into a solid polymeric product. Under the influence of azodi(isobutyronitrile), *N*-vinylindole forms a vitreous substance with a molecular weight in excess of 4000. Thus *N*-vinylindole is an active vinylpolymer capable of polymerising readily both by an ionic and a radical mechanism.

3. Copolymerisation and Activity Constants

Despite the large number of studies dealing with the copolymerisation of unsaturated monomers, so far little work of this kind has been done on the *N*-vinyl compounds of the pyrrole series. There is only one patent [140] which describes a method for the preparation of the copolymer of *N*-vinylpyrrole with tetrachlorodivinylbenzene and acrylonitrile in the presence of organic peroxides. For a long time there were no data whatever about the behaviour of *N*-vinylindole in the copolymerisation reaction.

Shostakovskii et al. [141] studied the free radical copolymerisation of *N*-vinylindole with methyl methacrylate and methacrylic acid. The reaction was carried out with different component ratios in the presence of azodi(isobutyronitrile) at 60°C for 100 h. The resulting copolymers had low molecular weights and a higher relative contents of *N*-vinylindole units than in the mixture of monomers. Potentiometric studies of the copolymers of *N*-vinylindole with methacrylic acid established that they dissociate like acids. The relative activity constants r_1 and r_2 were calculated from the copolymerisation data by a graphical method using the integral equation of Mayo and Lewis. It was found that $r_1 = 1.9 \pm 0.5$ and $r_2 = 0.42 \pm 0.1$ for the monomer pair *N*-vinylindole–methyl methacrylate and $r_1 = 1.43 \pm 0.05$ and $r_2 = 0.096 \pm 0.03$ for the monomer pair *N*-vinylindole–methacrylic acid. These constants confirm that in copolymerisation with methyl methacrylate and methacrylic acid *N*-vinylindole is the more active monomer.

N-Vinylindole retains maximum activity also in the copolymerisation with vinyl ethers. Domnina[89] studied for the first time the copolymerisation of *N*-vinylindole with butyl vinyl ether by ionic and radical mechanisms. Tin, iron, and aluminium chlorides were tested as cationic catalysts. It was shown that, as the amount of *N*-vinylindole in the initial mixture increases, there is an increase in the yield of the copolymer and a decrease in the amount of ether units in the latter. When the *N*-vinylindole : butyl vinyl ether ratio is 20 : 80, both monomers are incorporated in the polymeric chain in approximately equal amounts. Both solid and oily products are then obtained. Spectroscopic and chemical studies suggest the following structure of the principal copolymer units:



where $n > m$. Calculation gives $r_1 = 7.76 \pm 0.58$ for *N*-vinylindole and $r_2 = 0.12 \pm 0.007$ for butyl vinyl ether.

N-Vinylindole is of course the more active in the free radical interaction of these monomers. Thus in copolymerisation initiated by azodi(isobutyronitrile) products with compositions corresponding to component ratios of 90 : 10 and 85 : 15 are formed regardless of the initial component ratio. The low softening points of these copolymers, in the range 350–400°C, and their insolubility in many organic solvents are evidence of their high molecular weight.

Phenyl vinyl ether does not interact with *N*-vinylindole in the presence of cationic catalysts. In this case the polymerisation of each monomer separately takes place. However, phenyl vinyl ether, which does not show a tendency to radical polymerisation, copolymerises with *N*-vinylindole under the action of radical initiators[89].

The behaviour of *N*-vinylcarbazole in copolymerisation reactions has been studied in greater detail and there are more examples. The available literature data on the copolymerisation of *N*-vinylcarbazole with unsaturated hydrocarbons and also with vinyl and acrylic monomers are described below systematically and their practical applications are indicated. Thus polyisobutylene forms with 2% of *N*-vinylcarbazole a rubberlike product[142–149]. It can be vulcanised and, as regards stability to high temperatures, it surpasses polyisobutylene itself. Copolymerisation of *N*-vinylcarbazole with ethylene at 150–300°C under a pressure of 1500 atm in the presence of peroxide catalysts yielded products containing 70–95% of ethylene[146]. Polypropylene is also modified by being mixed with a preformed copolymer of ethylene and *N*-vinylcarbazole[147]. These products are very flexible and highly viscous, have a high tensile strength, and are used as gasket for the protection of glass from cracking. Copolymers of *N*-vinylcarbazole with triphenylethylene have been obtained by solid-state and emulsion polymerisation with peroxide catalysts[148]. *N*-Vinylcarbazole can be copolymerised with vinylphenol by the emulsion method in the presence of 20% H_2O_2 in polyepoxyethane and in the presence of sodium sulphate in sulphonated castor oil[149]. The copolymerisation of *N*-vinylcarbazole with styrenes and a mixture of styrene and acrylonitrile has been investigated in greater detail[33,149–152]. *N*-Vinylcarbazole interacts with styrene in the presence of 0.05–2 parts of alkanethiols and 0.1–10 millimoles of hydroperoxides obtained from di-isopropylbenzene, its halogeno-derivatives, phenylcyclohexane, and an equimolar amount of iron pyrophosphate at 30–40°C.[153] The styrene–*N*-vinylcarbazole copolymers exhibit high thermal stability (127°C) and low dielectric losses (0.00081).[149] Fluorostyrene and 3,4-difluorostyrene form with *N*-vinylcarbazole products which may be used as electrical insulators[154]. In the presence of 0.1% of benzoyl peroxide *N*-vinylcarbazole copolymerises with di(*p*-vinylphenyl)sulphide[155]. The copolymers of *N*-vinylcarbazole and *N*-vinylpyrrolidone[156] are used as stabilisers for hydrazine, fibre-forming compositions, and as adhesives for the improvement of the structure of soils. *N*-Vinylcarbazole forms with acrylonitrile[157,158] polymeric products in the presence of potassium persulphate at 80°C. On irradiation, it reacts with acrylate and methacrylate[159].

The capacity of *N*-vinylcarbazole to copolymerise with other monomers was characterised quantitatively for the first time in 1949 by Alfrey and Kapur[151] in copolymerisation with methyl methacrylate and styrene. Later in 1961 Hart[160] obtained improved values of these characteristics and calculated the specific activity Q and the polarity e.

Table 1. Activity constants for the copolymerisation of *N*-vinylcarbazole (M_1) with certain vinyl monomers (M_2).

M_2	r_1	r_2	Q_1	e_1	Refs.
Methyl methacrylate	0.040	2.0	0.20	−1.20	160
Methyl methacrylate	0.20	2.0	0.25	−0.56	151
Methyl acrylate	0.050	0.50	0.26	−1.32	160
Styrene	0.035	5.7	0.48	−2.07	160
Styrene	0.012	5.5	0.68	−2.45	151
Vinyl chloride	3.7	0.020	3.8	−1.01	160

According to Table 1, the copolymerisation constants show that in reactions with methyl methacrylate and styrene *N*-vinylcarbazole is the less active monomer. The polymeric radical with a terminal *N*-vinylcarbazole unit reacts much more rapidly with methyl methacrylate or styrene than with *N*-vinylcarbazole itself.

Table 2. Copolymerisation constants r_1 and r_2.

M_2	r_1	r_2	$r_1 \cdot r_2$
Vinyl formate	4.220±0.160	0.196±0.004	0.827
Vinyl acetate	3.020±0.240	0.152±0.018	0.465
Vinyl propionate	1.680±0.140	0.076±0.018	0.128
Vinyl butyrate	1.280±0.060	0.059±0.020	0.074

Chernobai et al.[161] made a spectrophotometric study of the copolymers of *N*-vinylcarbazole and methyl methacrylate. Ushakov and Nikolaev[162] studied the copolymerisation of *N*-vinylcarbazole with esters of vinyl alcohol and certain organic acids (formic, acetic, propionic, and butyric) in the presence of 0.5% of benzoyl peroxide. All the systems investigated have been characterised by the copolymerisation constants listed in Table 2.

The calculated copolymerisation constants r_1 and r_2 show that *N*-vinylcarbazole adds to the poly(*N*-vinylcarbazole) radical and to the polymeric chain with a terminal vinyl ester group much more rapidly than the second reaction component.

The experimental data accumulated so far are still insufficient to arrive at reliable conclusions concerning the reactivity of *N*-vinyl compounds of the pyrrole series in copolymerisation as a function of the characteristics of their structure. The number of studies dealing with quantitative calculations of the reactivity is extremely limited even for *N*-vinylcarbazole, the polymers of which are widely used in industry.

IV. CHARGE-TRANSFER COMPLEXES BASED ON PYRROLE, INDOLE, CARBAZOLE, AND THEIR VINYL HALOGEN-CONTAINING DERIVATIVES

The electron-donor properties of the nitrogen atom in the molecules of the heterocyclic compounds are responsible for their capacity to form complexes with various electron acceptors, including iodine, bromine, and chlorine. The study of the problem of intermolecular interaction has developed only recently. Intensive investigation of this problem has been additionally stimulated by the presence of semiconduction in a number of complexes and also by the fact that they can form as intermediates in many complex chemical reactions and biochemical processes [163-167]. The products of intermolecular donor–acceptor interaction are called charge-transfer complexes.

Blyumenfel'd et al. [168] state that such complexes are formed as a result of the redistribution of electron density in the system, leading to a negative charge at the acceptor and a positive charge at the donor. If the degree of transfer of an electron from one molecule to another is slight, the complex is unstable and easily decomposes into the initial molecules. If the interaction is very strong, then redistribution of electron density can lead to complete electron transfer with formation of either an ion pair or of two isolated species.

The theory of intermolecular donor–acceptor interaction was devised as late as the 1960's by Mulliken [169-173], who developed the quantum-mechanical concept of "complex mesomerism" put forward previously by Izmail'skii [174,175]. According to Mulliken's theory, the ground state of the complex is intermediate (mesomeric) between non-ionic and ionic structures, with the former predominating:

$$A + B \rightleftarrows [|\underline{A \ldots B}|] \longleftrightarrow [A^+ \ldots B^-|]$$

Transition to a higher state is accompanied by the appearance of a new intense long-wavelength absorption band, which is frequently the best characteristic of such complexes [176-178].

Aromatic amines and heterocycles with a nitrogen atom, which can be regarded both as π-electron and n-electron donors, constitute an interesting group of donors [179-181]. The study of charge-transfer complexes based on pyrrole compounds has assumed particular importance because they are often constituents of medicinal preparations. Among these compounds, indole derivatives merit most attention. A number of studies carried out by different investigators confirm the electron-donor properties of such compounds. The preparation of complexes of tryptophan or the corresponding indole derivatives with various biochemical electron acceptors containing isoalloxazine or pyridine rings has been described [182-185]. The capacity of indole to form complexes with many electron acceptors such as trinitrobenzene, *p*-benzoquinone, and chloranil is known [186]. A very stable charge-transfer complex of indole and iodine has been described recently [187].

Pullman and Pullman [1], who reviewed studies in quantum biochemistry, state that, judging from the energy coefficient of higher filled molecular orbitals, the electron-donor properties increase on going from pyrrole to indole and remain almost unchanged on going from indole to carbazole. Stable complexes with iodine are formed only by pyrrole and indole. Voronkov et al. [188] investigated by refractometric physicochemical analysis binary systems comprising monosubstituted benzenes of the type C_6H_5X (X = fluorine, chlorine, bromine, or iodine) with simple heterocycles, including pyrrole. They established that they are capable of forming 2 : 1 charge-transfer complexes. The authors concluded that such complexes are formed on the basis of the deviation from additivity of the isotherm and the colour change in the system. Electron transfer reactions with the tropylium cation, carbazole, and *N*-methylcarbazole have been investigated [189].

The studies of charge-transfer complex based on high-molecular-compounds, assumed great importance in the 1960's. [190] Hoegl et al. [190] obtained polymeric complexes based on polyvinyl aromatic, polyvinyl heterocyclic, and other compounds. The methods of their preparation have been described in several German and Belgian patents [191-194]. Hoegl devotes most attention [195,196] to the preparation of complexes based on polyvinylcarbazole. It was established that the latter reacts with nitro-compounds, acids (hydrogen chloride, malonic acid, phthalic acid), esters (dimethyl terephthalate), halogeno-compounds (tetrabromo-*p*-xylene, triphenylchloromethane, 9,10-dichloroanthracene), and quinones (chloranil and bromanil, phenanthrenequinone) [190].

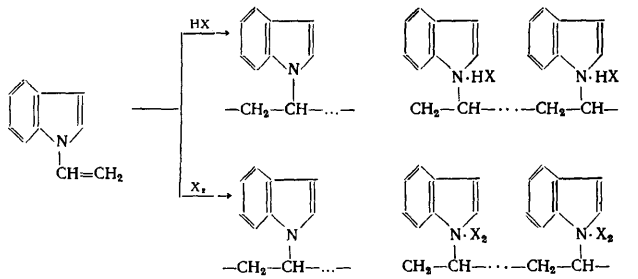
In 1965 Japanese investigators showed that polyvinylcarbazole forms at room temperature in chloroform solution complexes with tetracyanoquinodimethane [197], antimony pentachloride, and iodine [198]. All these products are deeply coloured and absorb in the visible part of the spectrum. Their resistivity is in the range 10^{-12}–10^{-16} Ω^{-1} cm^{-1}.

The solid-phase polymerisation of *N*-vinylcarbazole initiated by charge-transfer complexes of the monomer with acceptors such as Cl_2, Br_2, I_2, $SnCl_4$, and SO_2 is being investigated. Takakura, Okamura, and coworkers [199] made spectroscopic studies of these complexes.

In a more thorough investigation of the halogenation and hydrohalogenation of *N*-vinylindole, Shostakovskii and coworkers [200,201] showed that, instead of the expected products of the addition of the halogen to the double bond of the vinyl group, tetra- and hexamers of the halogeno-derivatives of *N*-vinylindole are mainly formed. It was established that chlorine, bromine, iodine, and the corresponding hydrogen halides readily add to *N*-vinylindole with formation of brightly coloured red, cherry-red, and brown powders which remain stable on storage and are also stable to acid and alkaline hydrolysis. The intense colour, the relatively high molecular weight, the variable composition of the compounds formed, and also the results of quantum-mechanical calculations indicating a relatively low ionisation potential of the *N*-vinylindole molecule led to the hypothesis that polymeric charge-transfer complexes are formed in this case. This is also confirmed by the appearance in the electronic spectra of the halogeno-derivatives of *N*-vinylindole of a broad band with a maximum in the regions 490–500 nm and 350–400 nm.

The fact that all the products of the halogenation and hydrohalogenation of *N*-vinylindole give rise to an ESR signal, which is absent from polyvinylindole, is important evidence for the formation of charge-transfer complexes. The sum of the data obtained suggests that, when halogens

and hydrogen halides react with *N*-vinylindole, the latter undergoes vinyl polymerisation with simultaneous formation of a charge-transfer complex by the following mechanism:



where X = Cl, Br, or I is a σ-electron acceptor component.

According to Mulliken's classification, these complexes may be regarded as the $n\pi\sigma$ type, but in their structure they should also be closer to the $\pi\sigma$ type than to the $n\sigma$ type.

Catalytic amounts of bromine, iodine, chlorine, and the corresponding hydrogen halides initiate the low-molecular polymerisation of *N*-vinylindole and also *N*-vinylcarbazole [121,129,201].

It has been shown that polyvinylindole also readily forms polymeric complexes of the type N...HX and N...X_2 which have a deep colour and give rise to ESR signals [201]. Their resistivity is in the range 10^{-14}–10^{-10} Ω^{-1} cm^{-1}.

Investigations have shown that the halogenation and hydrohalogenation of *N*-vinylindole is a fairly complex process. There are several competing reactions due to the presence in the *N*-vinylindole molecule of several active centres, including the double bond of the vinyl group and the unshared electron pair of the nitrogen atom.

Our earlier hypothesis that bromine adds to the vinyl group [95] appears to be improbable. Probably the same may be said of the work of Pielichowski [93,94], who is also more likely to have dealt with polymeric charge-transfer complexes than with products of the αβ-addition of fluorine, chlorine, bromine, and iodine to *N*-vinylcarbazole.

It follows from the literature data examined that *N*-vinyl compounds of the pyrrole series have been little investigated and are an interesting object for the study of the chemical properties of molecules with several reactive groups.

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Irkutsk Institute of Organic Chemistry, Siberian Division of the USSR Academy of Sciences

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The Mechanism of the Initiation of the Radical Polymerisation of Polar Monomers in Systems Comprising Organometallic Compounds

E.B.Milovskaya, L.V.Zamoiskaya, and E.L.Kopp

In the present review an attempt is made to examine from the same standpoint the reactions responsible for the development of radical polymerisation in systems comprising organometallic† compounds in combination with oxygen-containing derivatives (oxygen, hydroperoxides, acyl peroxide) or derivatives of variable-valence metals. Attention has been concentrated on systems effective at a low temperature. The causes responsible for the inhibition or total suppression of ionic-coordination polymerisation of polar monomers and favouring the development of the radical process in systems of the Ziegler-Natta type have been discussed. The bibliography includes 135 references.

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I. INTRODUCTION

An attempt has been made to use Ziegler–Natta catalysts, which have been successfully employed for the polymerisation of α-olefins, to polymerise other monomers, in particular polar monomers of the vinyl series. At first these attempts were unsuccessful: monomers such as vinyl acetate, methyl methacrylate, acrylonitrile, etc. could not be polymerised. Attempts were made to account for the absence of polymerisation by the breakdown of the catalyst in its interaction with the monomer. The development of studies on the interaction of these catalytic systems with vinyl monomers led to the creation of new initiating systems based on organometallic compounds and oxygen or peroxides capable of inducing radical polymerisation at reduced temperatures. On the other hand, the subsequent employment of the so called modified Ziegler catalysts also made possible the polymerisation of polar monomers.

II. SYSTEMS WITH AN ORGANOMETALLIC COMPOUND (OMC) AND AN OXYGEN-CONTAINING DERIVATIVE

1. Systems with an Organometallic Compound and Oxygen or a Hydroperoxide

It has been shown in a number of studies[1-12] that organic derivatives of Group II and III elements (zinc, cadmium, boron, and aluminium) alone give rise to hardly any polymerisation of polar monomers of the vinyl series; an effective process developed only in the presence of oxygen or peroxy-compounds.

The data presented in Tables 1 and 2 show that the most active of the systems investigated are those containing organoboron compounds in combination with oxygen or a hydroperoxide. The organoboron compounds can be arranged in the following sequence in terms of their activity[13]:

$$(n\text{-}C_4H_9)_2BOB(n\text{-}C_4H_9)_2 > B(n\text{-}C_4H_9)_3 > (n\text{-}C_4H_9)_2B(n\text{-}C_4H_9O) > > (n\text{-}C_4H_9)_2BBr > (n\text{-}C_4H_9)_2BCl$$

The overall activation energy found for a number of systems proved to be very low and comparable to the activation energy for the chain propagation reaction, which made it possible to carry out the process at reduced temperatures[8,12,14-16].

The copolymerisation constants obtained for a number of monomers suggested that radical polymerisation takes place in these systems[2,6,13,16,18,19].

Table 1. Polymerisation of polar monomers under the influence of the systems organometallic compound–oxygen.

Monomer	Process conditions: initiator type	initiator concn., M	10^2 × molar ratio O_2:OMC	time, h	t, °C	Yield of polymer, %	References
VA	$B(C_2H_5)_3$	$2.7\cdot10^{-3}$	14.3	20	30	40	13
MMA	ditto	$8\cdot10^{-2}$	6.5	~0.5	30.1	14	14
VC	$B(C_4H_9)_3$	$1.8\cdot10^{-2}$	9.5	3	20	20	15
AN	ditto	$4\cdot10^{-2}$	**	~0.8	0	4.2	16
VA	$Al(C_2H_5)_3$	$7\cdot10^{-2}$	50	24	25	12	4
VC	ditto	5*	***	4	−17	3	9
MMA	$Cd(C_2H_5)_2$	$5\cdot10^{-3}$	6.9	21	20	14	17

VA = vinyl acetate; MMA = methyl methacrylate; VC = vinyl chloride; AN = acrylonitrile.

*The concentration of $Al(C_2H_5)_3$ in petrol is expressed as a weight percentage; molar ratio VC : $(C_2H_5)_3Al$ = 7.28 : 1.

**In a sealed tube in air.

***Experiment carried out in a stream of dry and purified air flowing at a constant rate (50 ml min^{-1}).

Welch[2] believes that radicals cannot form as a result of the thermal decomposition of organometallic compounds of this type, since the polymerisation temperature is much below the range corresponding to the thermal decomposition of zinc and cadmium alkyls and boron and aluminium

† The Russian authors use the work "organoelemental" but since the term is not familiar in English and most of the compounds discussed are in fact metal derivatives, it has been replaced by "organometallic", especially since this is the term actually used in the title in the Russian version also (Ed. of Translation).

alkyls altogether fail to yield free radicals on thermal decomposition. The fact that the process can be carried out only in the presence of oxygen or peroxides[20] suggests that the stage preceding the generation of free radicals is the formation of peroxy-derivatives of the organometallic compounds.

Table 2. Polymerisation of vinyl chloride under the influence of the systems organometallic compound–peroxide[15].

Process conditions				Conversion, %	Degree of polymerisation	Activation energy, kcal mole^{-1}
catalyst, mole %	cocatalyst* mole %	t, °C	time, h			
$B(C_2H_5)_3$	13	room	several min	explosion		
1,79	42	−55	4	22.7	560	
	50	−65	68	61.4	400***	
	50**	−55	4	19.6	820	
$Al(C_2H_5)_3$	23	30	1	15.4	450	
1,89	50	−20	4	5.4		12.8
$Cd(C_2H_5)_2$	48	32	4.8	10.0		
2,5	»	22	19.0	10.0		16.0
	»	0	25.0	3.5		
$Zn(C_2H_5)_2$	48.5	4	1.5	25.6		
2,52	»	3	2.0	16.1		9.6
	»	−10	2.5	4.7		

*Cumenyl hydroperoxide, mole % relative to the catalyst.

**The part dissolved in tetrahydrofuran.

***t-Butyl hydroperoxide.

The synthesis and reactions of the organometallic compounds have been examined in detail by Sosnowsky and Braun[21], and therefore we shall note only some of their most important (as regards the present topic) reactions. The monoperoxides of cadmium, zinc, boron, and aluminium are extremely unstable at normal temperatures and readily undergo a number of heterolytic and homolytic reactions:

$$-MOOR- \xrightarrow{-MR} 2-MOR \quad (1)$$

$$-MOOR- \longrightarrow -M(OR)_2 \quad (2)$$

$$-MOOR- \longrightarrow -MO^{\cdot} + {}^{\cdot}OR \text{ (or } -MOO^{\cdot} + R^{\cdot}) \quad (3)$$

Alkoxy-derivatives are formed as a result of intermolecular exchange with the initial organometallic compound [reaction (1)][22-25] or by intramolecular exchange [reaction (2)][26,27].

Compounds which might form as a result of further reaction of the free radicals [reaction (3)] have also been identified[23]. The mixture of products formed in the presence of the peroxides of trivalent elements is still more complicated, since diperoxides can also participtae in reactions (1)–(3). For example in the oxidation of organoboron compounds homolytic decomposition takes place to the greatest extent precisely at this stage[23]. A general parallel may be drawn[28] between the ease of the auto-oxidation of organoboron compounds and the capacity of any group to transfer electrons to the unfilled boron orbital, making it less sensitive to attack by oxygen. The activity series of organoboron compounds,

$$BR_3 > R_2BOR > RB(OR)_2 \text{ and } BR_3 > R_2BCl > RBCl_2$$

in oxidation reactions are determined by the overlapping of the boron orbitals by those of chlorine or oxygen. The reactivity of organoboron compounds in oxidation corresponds to their activity in polymerisation processes[13]. The oxidation of organoaluminium compounds and further reactions of peroxides take place even more vigorously than with organoboron compounds[23,27,29]. The only stable peroxides proved to be $Al(OR)_2OOR$, which were isolated and characterised[30]. The fact that the reactions of the peroxy-derivatives of organoaluminium compounds involve a stage with formation of free radicals was demonstrated under model conditions[4] and confirmed by showing that polymerisation in the presence of these peroxides is possible[30]. The peroxy-compounds obtained beforehand at a low temperature are then capable of initiating polymerisation when the monomer is introduced[31]. However, the activity of these pre-formed peroxides is much lower than that of systems which initiate polymerisation by peroxides *in statu nascendi*. In the first case the process develops at temperatures normal for radical initiation‡ and in the second it actually takes place at very low temperatures down to −65°C (for example, with boron compounds).

This phenomenon was explained by the existence of "active" peroxide, since it was established that ethereal solutions of the peroxide rapidly lose their catalytic activty although the peroxide concentration determined iodometrically did not change[31]. It was suggested that the low-temperature polymerisation is initiated by the free radicals formed as a result of a kind of redox reaction between the initial organometallic compound and its peroxide[9,14,33-35].

Bawn et al.[33] showed that in the polymerisation of methyl methacrylate in the presence of $(C_4H_9)_3B-O_2$ neither the peroxide (obtained from part of the boron alkyl) nor the organoboron compound by itself are capable of initiating the low-temperature polymerisation. In a kinetic study they established the following dependence of the reaction rate on the concentrations of the monomer, peroxide, and the initial boron alkyl:

$$V = k_{obs}[M][ROOBR_2]^{1/2}[Br_3]^{1/2}.$$

A mechanism for the formation of free radicals was proposed on the basis of the hypothesis that the reaction is a free radical process. Initially a monomer–boron alkyl complex is produced:

$$BR_3 + M \rightleftarrows BR_3\dot{M}. \quad (4)$$

Equilibrium is established rapidly and is displaced to the right so that the concentration of the complex is almost equal to the initial concentration of tributylboron. Then, in bimolecular redox reaction (5), the initiating radicals are produced:

$$BR_3\dot{M} + R_2BOOR \rightarrow R_3BMRO^{\cdot} + R_2BO^{\cdot}. \quad (5)$$

The authors assume that chain propagation and termination take place as in an ordinary free radical process. The dependence of the rate of initiation on the concentrations of the initiator components obtained from Eqns. (4) and (5) and the variation of the overall rate of the process with the same concentrations found on this basis agree with the experimental findings. These hypotheses might be confirmed by data on the polymerisation kinetics of monomers of low polarity, in particular vinyl chloride. Then the equation for the rate of the process should differ from the corresponding expression for highly polar monomers. Unfortunately Bawn et al.[33] do not present data of this kind.

Talamini and Vidotto[8] believe that the monomer does not participate in the initiation step, since the activation

‡ The period of 50% decomposition of a 1% solution of boron peroxide in octane is 4.3 and 1.5 h at 50° and 100°C respectively; at 25°C the content of the peroxide does not change over a period of 50 h.[32]

energy for initiation under the influence of $(C_4H_9)_3B-O_2$ is the same in the polymerisation of vinyl chloride (a monomer of low polarity) and the highly polar methyl methacrylate§.

Welch[14] believes that the redox reaction between the oxidised and unoxidised forms of the organoboron compound does not require the initial formation of the complex of R_3B with the monomer. The experimental findings for polymerisation agree with the proposed mechanism for the generation of free radicals: the overall rate of the process and the conversion are higher when the concentrations of the boron alkyl and oxygen do not differ very much:

$$BR_3 + O_2 \rightarrow R_2BOOR, \quad (6)$$

$$BR_3 + R_2BOOR \rightarrow BR_3 + R_2BO^{\cdot} + RO^{\cdot}. \quad (7)$$

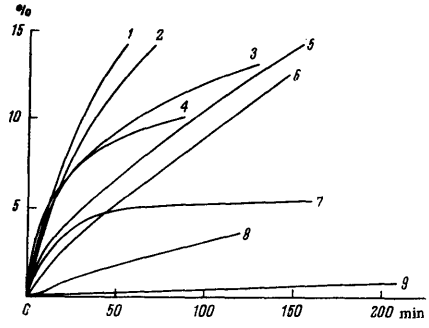


Figure 1. Polymerisation of methyl methacrylate at 30°C in the presence of a constant concentration $[(C_2H_5)_3B]_0 = 7.18 \times 10^{-3}$ M and a variable concentration $[O_2]_0$ (10^{-3} M): 1) 3.36; 2) 1.97; 3) 4.47; 4) 1.14; 5) 5.4; 6) 6.65; 7) 0.51; 8) 7.89; 9) 0.0.

When $[O_2] \gg [R_3B]$, the entire boron alkyl is oxidised to the peroxide and reaction (7) is impossible. When the concentration ratio is reversed, the peroxy-compound is rapidly exhausted, which leads to the decay of the process at a low conversion. From a study of the polymerisation kinetics of methyl methacrylate with $(C_2H_5)_3B-O_2$, Hansen[34] showed that the process can be described by simple relations only at the very beginning. This is because in systems of this type a number of competing reactions take place and lead to the formation of free radicals. The rates of these reactions are different and are determined by the relative amounts of the starting reactants. Figs. 1 and 2 present the kinetic curves obtained for various concentrations of one of the initiating components. The maximum rate occurs when $[R_3B] > 2[O_2]$, but it then falls rapidly as a result of the complete reduction of the peroxide. Under the condition $[O_2] < [R_3B] < 2[O_2]$ the system contains, together with the initial boron alkyl, its hydroxy-form, which is a weaker reducing agent and gives rise to slow and prolonged generation of free radicals at a constant rate:

$$\rangle BOOR + \rangle BR \xrightarrow{fast} R^{\cdot} + (BO^{\cdot}) \quad (8)$$

$$\rangle BOOR + \rangle BOR \xrightarrow{slow} R^{\cdot} + (BO^{\cdot}). \quad (9)$$

The homolytic dissociation of the peroxide bond as a result of the redox reaction was studied under model conditions by Hansen and Hamann[37]. When iodine was used as a free radical acceptor, they established that the interaction of the peroxide with the unoxidised boron alkyl is a reduction process with a stoichiometric ratio close to unity. The formation of ethyl radicals (the only ones reliably demonstrated) does not take place in each step of the interaction in consequency of reduction in the "cage":

$$\begin{array}{l} B-C_2H_5 \\ \uparrow \\ C_2H_5O-O-B\rangle \end{array} \rightarrow \rangle B-OC_2H_5 + C_2H_5^{\cdot} + \rangle BO^{\cdot}. \quad (10)$$

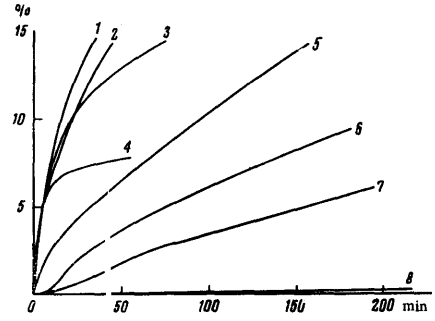


Figure 2. Polymerisation of methyl methacrylate at 30°C in the presence of a constant concentration $[O_2]_0 = 5.4 \times 10^{-3}$ M and a variable concentration $[(C_2H_5)_3B]_0$ (10^{-3} M): 1) 21.5; 2) 71.8; 3) 14.3; 4) 35.5; 5) 7.18; 6) 5.38; 7) 3.6; 8) 1.43; 9) 0.0.

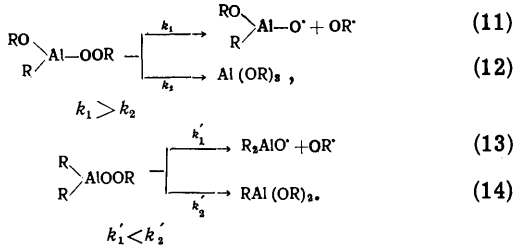
The emergence of the radicals from the "cage" initiates the free-radical processes; the reaction in the "cage" results in the formation of alkoxy-compounds. In agreement with the data obtained under model conditions, a very small boron content was found in the polymer[34].

Furukawa and coworkers[31] showed that systems based on alkoxy-derivatives of zinc in combination with peroxides are more active than those based on zinc alkyls. The latter are weak Lewis acids[38]; this is even more true of the alkoxy-derivatives of zinc, which makes it unlikely that its complex with an electron-donor monomer is formed as a result of reaction (4).

The findings for systems with organoaluminium compounds suggest that in this case too the active polymerisation initiators at low temperature are systems based on monoalkoxydialkylaluminium and oxygen or a hydroperoxide This is confirmed[9,35] by the absence of the polymerisation of vinyl chloride when the system $(C_2H_5)_3Al-O_2$ contains little oxygen and the impossibility of the polymerisation of vinyl acetate under the influence of the system $(C_2H_5)_3Al$–isopropylphenyl hydroperoxide[4]. These findings show that, of the two possible modes of the process: decomposition with formation of free radicals or rearrangement into

§ In the determination of the activation energy for the initiation reaction the value $E_{prop} - \frac{1}{2}E_{term} = 1.5$ kcal mole^{-1} was employed[8]. However, the value of $E_{prop} - \frac{1}{2}E_{term}$ found for vinyl chloride in a number of studies varied from 1.5 to 5 kcal mole^{-1}, [36] and therefore the identity of the activation energies for the initiation reaction found by Bawn[33] and Talamini[8] is purely fortuitous.

an alkoxy-compound, the first takes place with organic derivatives of alkoxyperoxyaluminium [reaction (11)] and the second takes place with the alkylperoxy-derivatives [reaction (14)]:



(11)

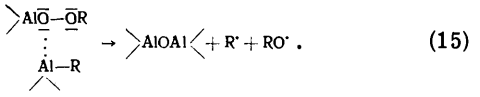
(12)

(13)

(14)

This kind of inversion of rate constants can be explained by the fact that the RO group reduces the electron deficit of the aluminium atom and thus electrons are shifted to the peroxide bond, facilitating its dissociation. On the other hand, in the alkyl peroxide the withdrawal of electrons from the peroxide bond hinders its dissociation and, together with the electron-acceptor properties of the aluminium atom, leads to rearrangement with formation of an alkoxy-derivative. These hypotheses can explain the experimental observations regardless of whether the decomposition of the peroxide is a mono- or bi-molecular process.

Razuvaev and coworkers [35] attributed the formation of free radicals to a redox reaction of the type



(15)

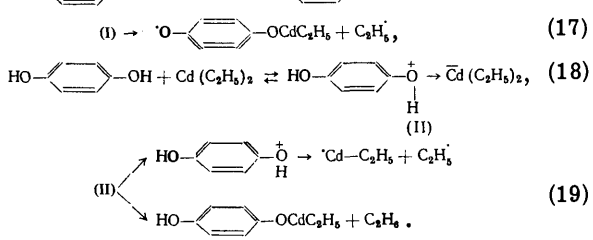
The formation of the R$^{\cdot}$ radical (R = ethyl) was confirmed by the analysis of the gaseous compounds evolved; the RO$^{\cdot}$ radicals were detected in the form of the terminal groups in the polymer.

The results show that the conclusion that polymerisation with organometallic compound–oxygen or hydroperoxide systems has a radical mechanism is fairly well founded. However, the chemistry of the initiation process, in particular the nature of the initiating radicals and the participation of the monomer in this reaction, involves many contradictions. We may note that in the absence of oxygen, boron alkyls are capable of initiating very slow polymerisation of styrene, acrylonitrile, and 1,1-dichloro-2-fluoroethylene, but not vinyl acetate [3].

Hydroquinone does not inhibit this process, which, according to Hansen [34], is evidence of the occurrence of ionic polymerisation. The polymerisation of methyl methacrylate under the influence of (iso-$C_4H_9)_3Al$ and (iso-$C_4H_9)_2Al$.(iso-C_4H_9O) takes place in the absence of oxygen at 60°C and an initiator concentration of 10 mole % relative to the monomer [39]. It was shown that the polymerisation of methyl methacrylate also takes place with $(C_2H_5)_3Al$. [40] The poly(methyl methacrylate) formed has a structure characteristic of polymers produced under the influence of $(C_2H_5)_4CaZn$ and (n-C_4H_9)Li. [41] We may note that extremely large amounts of the catalyst (up to 30% relative to the monomer) are employed in these investigations [39,40]. This leads to the binding of a considerable proportion of the monomer in a complex with the organoaluminium compound (via the carbonyl oxygen), which results in a decrease of electron density at the double bond. Under these conditions, there is a possibility of anionic polymerisation even under the influence of an initiating agent as weak as R_3Al.

2. Systems with Metal Alkyls and Oxygen-Containing Compounds (Quinones, Phenols, and Acyl Peroxides).

Unusual redox systems based on combinations of organometallic compounds and quinones or phenols have been studied by Furukawa et al. [17] The most notable effect was observed in the polymerisation of methyl methacrylate under the influence of $(C_2H_5)_2Cd$–quinone (or phenol) systems. The activity of such systems decreases as a function of the nature of the metal alkyl in the series $R_2Cd > > R_2Zn > R_3Al$. The formation of free radicals is attributed to reaction (16) and (17) in the case of a quinone and (18) and (19) in the case of a phenyl:



(16)

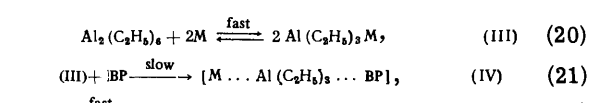
(17)

(18)

(19)

As a result of electron transfer from oxygen to cadmium, unstable addition products (I) or (II) are formed, their decomposition being accompanied by the formation of free radicals.

Milovskaya and coworkers [42–45] obtained systems comprising aluminium alkyls and acyl peroxides capable of initiating the polymerisation of polar monomers (vinyl acetate, methyl methacrylate, acrylonitrile). The process obeys the laws of free-radical polymerisation and occurs much below the temperature of the thermal decomposition of the corresponding peroxides. The step involving the formation of free radicals is unusual in this case and different from the processes occurring in organometallic compound–hydroperoxide systems. The interaction between $(C_2H_5)_3Al$ and benzoyl peroxide (BP) takes place very vigorously in the absence of the monomer by a donor–acceptor mechanism with a stoichiometric ratio of 2:1. Under the experimental conditions, this reaction does not stop at the stage involving the formation of the complex and results in the formation of the following final products: diethylaluminium benzoate and gaseous compounds derived from various reactions of the ethyl radical [46]. An obligatory condition for the occurrence of polymerisation is the participation of the polar monomer in the formation of an intermediate complex [42]. The sum total of the information obtained under model conditions and in polymerisation suggests that free radicals are formed in the following reactions [47]:

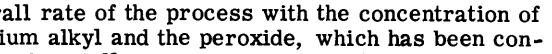


(III) (20)

(IV) (21)

(22)

The relation between the rate of initiation and the concentration of the components of the initiating systems obtained from Eqns.(20)–(22) leads to an expression for the variation of the overall rate of the process with the concentration of the aluminium alkyl and the peroxide, which has been confirmed experimentally:



The capacity for complex formation of monomers which are weak electron donors, such as styrene or vinyl chloride, has proved insufficient for the occurrence of polymerisation under the influence of the system $(C_2H_5)_3Al$–acyl peroxide. In this case, for polymerisation to occur, it is necessary to introduce complex-forming agents such as an ether or ester or acetonitrile[47,48]. The results of studies on the kinetics of the polymerisation of vinyl chloride with the system $(C_2H_5)_3Al$–benzoyl peroxide (BP)–ethyl acetate (EA) show that the step involving the formation of free radicals is different in this case from the corresponding reactions in the polymerisation of polar monomers. The expression for the total rate of polymerisation is

$$V = k[M]^n\left[\frac{Al(C_2H_5)_3}{\ni A}\right]^{1/4}[BP]^{1/4},$$

from which it follows that the non-complex form of the organoaluminium compound participates in the stage involving the formation of free radicals; the stoichiometric ratio of the components of the catalytic system is the same as in the model system (without monomer):

$$Al_2(C_2H_5)_6 + 2\,EA \rightleftarrows 2\,Al(C_2H_5)_3\cdot EA, \qquad (23)$$

$$2\,Al(C_2H_5)_3 + BP \xrightarrow{k_1} 2\,C_6H_5COOAl(C_2H_5)_2 + 2\,C_2H_5^{\cdot}. \qquad (24)$$

The observed difference in the behaviour of the complex-forming agents and polar monomers is evidence that the function of the latter (in the free radical formation stage) is not restricted solely to the role of complex-forming agents. Probably the displacement of the monomer by benzoyl peroxide from the complex $(C_2H_5)_3Al.M$ [reactions (21) and (22)] is accompanied by the interaction of the benzoate radical with the double bond (a reaction in the "cage"). This is reflected in a change of the stoichiometric relation between the components of the catalytic system established under model conditions[46] and in the polymerisation of polar monomers[43-45].

The fundamental difference between the mechanisms of the formation of free radicals in systems with participation of hydroperoxides and acyl peroxides is well illustrated by the dependence of the efficiency of the system on the nature of the organoaluminium compounds and monomers employed. In the formation of initiating systems based on acyl peroxides one can use only aluminium alkyls but not alkoxy-derivatives, which are weak Lewis acids and show no tendency to react with electron-donor compounds[42,44,47,49]. On the other hand, in combination with a hydroperoxide, active systems have been obtained only with mono- and dialkoxy-derivatives of aluminium and the electron–donor capacity of the monomer is not an essential condition for the process to occur[4,9,35].

The phenomenological conditions necessary for the development of the polymerisation process with participation of the system R_3Al–acyl peroxide corresponds most closely to the conditions which obtain in the polymerisation of polar monomers with modified Ziegler catalysts. Consequently systems of the first type can be regarded to some extent as models for more complex multi-component systems[50]. Razuvaev and coworkers[51] established that systems based on di-isopropylmercury and benzoyl peroxide are active initiators of the polymerisation of methyl methacrylate and vinyl chloride. The process kinetics indicate free radical polymerisation; the authors believe[52] that the formation of free radicals can probably be attributed to reactions analogous to those proposed in the study of the interaction of the above components under model conditions. The system with the organomercury compound is much less active than that obtained on the basis of aluminium alkyls.

III. SYSTEMS WITH A METAL ALKYL AND A VARIABLE-VALENCE METAL DERIVATIVE

The polymerisation of polar monomers of the vinyl series can be achieved successfully with the so called modified Ziegler catalysts. At the present time there is no single view concerning the mechanism of the process, i.e. whether they are of the radical or ionic-coordination type. Nevertheless the literature data show that there is better evidence for a radical mechanism.

In many cases the catalyst is modified by the introduction into the reaction system of a polar solvent[53-55]. Furukawa and coworkers[54,55] showed that polar monomers such as vinyl acetate or methyl methacrylate themselves behave as polar solvents. Although a rational approach to the choice of the catalytic pair does not exist, nevertheless a necessary condition for the process to occur is the separation of the catalyst components by a complex-forming agent (the monomer or solvent)[54].

Table 3. Activity of the catalytic systems metal alkyl–metal halide in the polymerisation of polar monomers* [54].

Catalyst	Monomer	t, °C	Time, h	Conversion, %
$(C_2H_5)_2Zn$–$VOCl_3$	MMA**	20	24	82
$(C_2H_5)_2Zn$–$FeCl_3$	MMA*	20	24	90
$(C_2H_5)_2Zn$–VCl_4	VA	20	24	56
$(C_2H_5)_2Cd$–VCl_4	VA***	20	27	39
$(C_4H_9)_2Hg$–$BiCl_3$	MMA	15	50	86
$(C_2H_5)_3Al$–VCl_4	VA	20	40	36

*5 ml of solvent; 2 mole % of metal alkyl; 1 mole % of metal halide; 5 ml of monomer.

**The solvent was hexane and in the remaining cases dioxan.

***3 ml of monomer and 1.5 ml of solvent.

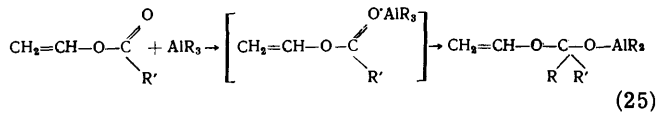
Table 3 presents certain data for the polymerisation of a number of polar monomers under the influence of systems metal alkyl–metal halides. In all cases the components are introduced in a specified order: the metal halide (MX) first, then the monomer, and finally the metal alkyl (RM).

When the order was altered, MX followed by RM and then by the monomer, polymerisation did not occur; this feature differs sharply from the behaviour of the catalytic system in the polarisation of non-polar monomers[54].

Table 4 presents data for the effect of the solvent on the activity of the catalytic system $(C_2H_5)_3Al$–VCl_4.[55]

At present it is not clear why the nature of the monomer affects the relative positions of complex-forming compounds in the activity series (Table 4). The data for the variation of the rate of the process when the order of mixing of the reacting compounds is altered in any way show that in the catalytic system $(C_2H_5)_3Al$–$VOCl_3$ both components are involved in complex formation, but the complex-forming capacities of vinyl and ethyl acetates are by no means equivalent[55]. A similar conclusion is valid also for the system $(C_2H_5)_3Al$–VCl_4 (see Table 4). It may be

supposed that this difference is associated with the irreversible consumption of part of the organoaluminium component by its interaction with the monomer:



(25)

Table 4. Effect of solvent on the activity of the system alkylaluminium–vanadium halide[55].

Monomer	Solvent	Conversion, %	Monomer	Solvent	Conversion, %
VA	n-hexane	4	MMA	n-hexane	2
	toluene	4		toluene	2
	ether	14		ether	7
	tetrahydrofuran	39		tetrahydrofuran	67
	dioxan	29		dioxan	61
	ethyl acetate	61		ethyl acetate	28
	ethanol	traces			
	acetone	traces			

Note. Experimental conditions: 5 ml of monomer, 1 mole % $(C_2H_5)_3Al$, 0.25 mole % $[VCl_4]$, 1 ml of n-hexane as solvent for the catalyst, 4 ml of solvent, room temperature, duration 24 h; order of mixing: (1) metal halide, (2) solvent, (3) monomer, (4) $(C_2H_5)_3Al$.

The occurrence of such reactions has been established for organocadmium compounds[56]. In order to elucidate the mechanism of the effect of such systems, a study was made of the copolymerisation of methyl methacrylate with styrene and of vinyl acetate with styrene using catalysts of the type RM–MX (where M in RM is cadmium, zinc, or aluminium and MX is $VOCl_3$, VCl_4, or $TiCl_4$). It was found that the composition of the copolymer is the same as in a radical process[54,57]. To confirm the radical mechanism of the polymerisation, the ESR method was also employed[54]. In the spectrum of the system ethylene dimethacrylate–$(C_2H_5)_2Zn$–$HgCl_2$ or ethylene dimethacrylate–$(C_2H_5)_2Cd$–$HgCl_2$ the same signals were observed as in the polymerisation of the same monomer under the influence of azobis(isobutyronitrile). On the basis of the data obtained, hypotheses were put forward concerning the free radical mechanism of the polymerisation of polar monomers on Ziegler catalysts[54,55,57].

One may add that in a number of studies[58,59] the possibility of the polymerisation of acrylonitrile and methyl methacrylate under conditions in which the components of the Ziegler catalyst were mixed before the addition of the monomer has been demonstrated.

The catalytic systems $(C_2H_5)_3Al$–$TiCl_4$ and $(C_2H_5)_3Al$–$Ti(OR)_4$, maintained at 0° and 30°C respectively, were used to polymerise methyl methacrylate[58,59]. In view of the enhanced content of the polymer with the syndiotactic structure (92% against 84% in the radical process), the authors concluded that non-radical polymerisation occurs in this case.

Acrylonitrile has been polymerised using the system $(C_2H_5)_3Al$–$VOCl_3$ maintained at 25°C for 20 min[60]. According to infrared spectroscopic data, the resulting polymer (M = 2325) had a structure different from that expected for a radical process.

Much attention has been devoted to the elucidation of the possible use of catalytic systems of the Ziegler–Natta type in the polymerisation of vinyl chloride. The choice of catalytic systems in this case is complicated by the fact that metal alkyls, and in particular aluminium alkyls, are capable of reacting irreversibly with the chlorine-containing monomer and the polymer[61–63]. Organoaluminium compounds are known[64–66] to take part in the reaction

$$AlR_3 + R'X \rightarrow R_2AlX + R'{-}R \qquad (26)$$

more or less readily depending on the structure of the initial compound and that of the halogeno-derivative. In many cases the process goes to completion and results in the formation of aluminium trichloride—a typical cationic catalyst. In the presence of a variable-valence metal halide, aluminium halide formed by the reaction

$$MX_n + AlR_3 \rightarrow RMX_{n-1} + R_2AlX \qquad (27)$$

reacts subsequently even more readily with the chlorine-containing component[62].

Modified catalytic systems suitable for the polymerisation of vinyl chloride differ from the classical Ziegler–Natta catalysts by the fact that they include either an organometallic compound with reduced reactivity or complex-forming agents capable of altering to some extent the nature of the catalyst components.

Table 5. Polymerisation of vinyl chloride by modified metal alkyl–metal halide catalysts[68].

Catalyst	Molar ratio triethylamine : organoaluminium component	Yield, g $TiCl_3$	$[\eta]$
iso-$C_4H_9)_2Al$ (i-C_4H_9O)–$TiCl_3$*	—	34.1	0.36
ditto	0.23	33.0	0.15
»	1.35	8.1	—
$ClAl(OC_2H_5)$ (C_2H_5) – β-$TiCl_3$**	—	11.4	0.13
ditto	0.2	26.6	0.14
$BrAl(OC_2H_5)$ (C_2H_5) – β-$TiCl_3$**	—	10.8	0.1
ditto	0.2	27.0	0.18
»	0.39	25.3	0.24
»	0.58	29.5	0.18
»	0.97	19.3	—

*Temperature 60°C, solvent—petrol.
**Temperature 60°C, solvent—benzene.

Razuvaev and coworkers[67–70] must be regarded as pioneers in the field of vinyl chloride polymerisation on complex catalysts. They employed as components of the catalytic system organic derivatives of alkoxyaluminium or an alkoxyalkylaluminium halide combined with Ti^{4+} and Ti^{3+}. The data in Table 5 show that very active catalytic systems can be obtained by a suitable choice of components.

It is interesting to note that there exists an optimum ratio of the complex-forming agent (CFA) and the organoaluminium compound, namely CFA : Al < 1, for which the yields and the molecular weights of the polymer are maximum.

It is believed[68,69] that a necessary condition for the activity of the catalytic system is the presence of an organoaluminium compound in a free state. It has been shown that in the polymerisation of vinyl chloride on modified catalysts the same rules hold as for non-polar monomers (for example, the polymeriastion of propene is influenced by electron-donor additives[71,72]). It is thought[67–70] that this is evidence of the occurrence of an ionic-coordination

process. The improved crystallinity of poly(vinyl chloride) obtained on the heterogeneous catalyst $(C_2H_5)_3Al-TiCl_3-CFA$ compared with the polymer synthesised using radical initiators is quoted by the authors as confirmation of their view. However, it has been established that all poly(vinyl chloride) specimens of low molecular weight show high crystallinity regardless of the method of their preparation[73,74]. Thus the fact of improved crystallinity alone cannot be unambiguously interpreted, since the polymers obtained had $[\eta] = 0.1-0.2$.

Ashikari[75-77] investigated as catalysts for the polymerisation of vinyl chloride a number of catalytic systems of the type $(C_2H_5)_3Al-MX-MC$, where MX is the halide of a variable-valence metal (titanium, iron, vanadium, etc.) and MC is the modifying component (butanol, tetrahydrofuran, dibutyl sulphide, ethyl acetate, acetone). Fig. 3 shows the relation between the rate of polymerisation and the MC : Al ratio for the system $(C_2H_5)_3Al-VCl_3$. Depending on their effect on the rate of the process, the modifying components can be clearly divided into two groups. The first includes butanol, tetrahydrofuran, and dibutyl sulphide which give rise to a distinct maximum in terms of the variables investigated. With butanol, the maximum effect at MC : Al = 3 was attributed[75-77] to the formation of trialkoxyaluminium which is more active in the formation of the catalyst than the initial alkyl. Thus we may note that, for systems with titanium tetrachloride, dialkoxyaluminium derivatives are no longer active as co-components[68]. The maximum rate at MC : Al $\geq$ 1 in the presence of tetrahydrofuran or dibutyl sulphide has been explained[75-77] by the participation in the process of the complex form of the organoaluminium compound. The monotonic increase of the rate in the presence of ethyl acetate is probably associated with the formation of an alkoxy-compound:

$$R-\underset{\underset{OR}{|}}{\overset{\overset{O}{\|}}{C}} + Al(C_2H_5)_3 \rightarrow R-\underset{\underset{C_2H_5}{|}}{\overset{\overset{OAl(C_2H_5)_2}{|}}{C}}-OR \quad . \qquad (28)$$

The occurrence of this type of reaction is extremely likely, since the process was carried out at 40°C. A similar reaction can also take place in the presence of acetone which reacts in the enol form with organoaluminium compounds[78]. In this case too a monotonic increase of the rate was observed with increasing concentration of the modifying agent MC. The lack of an effect on the structure of the polymers produced and also the similarity of the copolymerisation constants of vinyl chloride and acrylonitrile to the usual constants for radical processes lead to the hypothesis of the occurrence of radical polymerisation and the influence of systems of the type $(C_2H_5)_3Al-MX-MC$.[77]

One may add to this that, on the basis of the copolymerisation constants of vinyl chloride and vinyl acetate, Baker[79] regards copolymerisation under the influence of the system $(iso-C_4H_9)_3Al-VOCl_3$ as a radical process.

Systems consisting of alkoxyaluminium compounds and various derivatives of variable-valence metals have been investigated by Giannini and Ceska[80]. The system $(C_2H_5)\cdot AlCl(OC_2H_5)$–vanadium oxide acetylacetonate proved to be the most active; vinyl chloride was polymerised down to temperatures as low as −78°C. The kinetic method was employed to elucidate the mechanism of the action of this catalyst. It was established that the variation of the reciprocal of the degree of polymerisation with the solvent : monomer ratio resembles the corresponding relation in a radical process.

On the basis of these results and the copolymerisation of constants of vinyl chloride and vinyl acetate, it was concluded that the process is of a free radical type. The authors see confirmation of this view[80] also in the fact that the structure and properties of the polymer obtained in the presence of the above catalytic systems and in radical polymerisation (at the same temperatures) are identical. When the reaction was performed under model conditions (in the absence of the monomer), the formation of gaseous compounds (ethane and butane) was observed and was attributed to the occurrence of free radical stages. The participation of ethyl radicals in the initiation step was also established by the finding that a polymer with labelled terminal groups is formed when a labelled organoaluminium component is employed (it was shown that chain transfer to aluminium does not take place). Effective catalytic systems for the polymerisation of polar monomers were obtained by Yamazaki and coworkers[81,82] using titanium tetrabutoxide in combination with organoaluminium compounds. The latter can be arranged in the following series in terms of their activity as co-components of the catalyst: $(C_2H_5)AlCl_2 \gg (C_2H_5)_2AlCl > (C_2H_5)_3Al > AlCl_3 > (C_2H_5)_2\cdot Al(OC_2H_5)$.

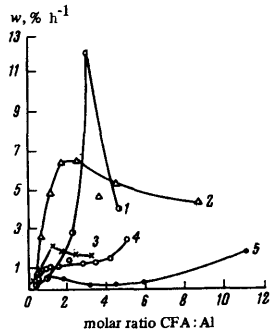


Figure 3. The effect of the nature and concentration of the complex-forming agent (CFA) on the rate of polymerisation of vinyl chloride at 40°C in the presence of the system $(C_2H_5)_3Al-VCl_3$; molar ratio Al : V = 1.37: 1) butanol; 2) tetrahydrofuran; 3) dibutyl sulphide; 4) ethyl acetate; 5) acetone.

Attention was concentrated on the polymerisation of vinyl chloride with the most active system $(C_2H_5)AlCl_2-Ti(OC_4H_9)_4$. In view of the absence of both the inhibiting effect of diphenylpicrylhydrazyl and of the effect of carbon tetrachloride as a chain-transfer agent (carbon tetrachloride did however accelerate the process) and the difference between the copolymerisation constants of styrene and vinyl chloride on the other hand and the values characteristic of radical processes on the other, it was concluded that the reaction occurring under the influence of this system (and other similar systems) is most likely to have an ionic-coordination mechanism[81,82]. For our part, we may note that many facts are fairly consistent with the hypothesis of the radical nature of the process or at least they do not contradict it. The absence of the effect of diphenylpicrylhydrazyl can be probably attributed to the higher rate of the donor–acceptor interaction ($\rangle N \rightarrow Al\langle$) than that of the reaction with participation of an unpaired electron. Furthermore, it was established that carbon tetrachloride is not a chain-transfer agent in the radical polymerisation

of vinyl chloride[83]. The interaction of organoaluminium compounds with carbon tetrachloride takes place via a free radical formation stage[84]¶, which may in fact be responsible for the acceleration of polymerisation[81,82] in the presence of carbon tetrachloride.

Budanova and Mazurek[88] made a detailed study of the kinetics of the polymerisation of vinyl chloride with $Ti(OC_4H_9)_4$–$(iso\text{-}C_4H_9)_2AlCl$, which is very similar to those discussed above[81,82]. They established that the dependence of the rate of polymerisation on the concentration of the components of the initiating system and the rate of formation of Ti^{3+} under model conditions are consistent with a typical radical reaction with bimolecular chain termination. The variation of the reciprocal of the degree of polymerisation with the rate of the process is characteristic of free-radical initiation. The ratio k_{term}/k^2_{prop} obtained proved to be equal to the value quoted for radical initiation[89].

One of the proofs for the ionic-coordination polymerisation of vinyl chloride on modified Ziegler catalysts is the possibility of copolymerising it with propene[82,90]. However, Imoto and coworkers[91] established that vinyl chloride copolymerises with propene also under the influence of radical initiators [azobis(isobutyronitrile)]; as a result, the very fact of the formation of the copolymer in the system metal alkyl–metal halide cannot be interpreted unambiguously. One could postulate that in the case of modified Ziegler catalysts two processes take place: one, with an ionic-coordination mechanism, leads to the formation of polypropylene and the other has a radical mechanism involving the participation of vinyl chloride. The formation of the copolymer may be regarded as a result of the generation of a radical centre in the main chain of the polypropylene, which then initiates the grafting of vinyl chloride or recombines with the growing poly(vinyl chloride) radical.

The results of studies of the polymerisation of polar monomers with many modified catalysts show that the concept of the development of a radical process is in this case fairly well founded[54,55,57,77,79,80,88].

We shall now examine the problem of what reactions between the components of the Ziegler catalyst lead to the formation of free radicals. Unfortunately there are almost no literature data on the interaction between the components of the initiating systems effective in the polymerisation of polar monomers; systems which are relatively inactive in such processes have been mainly examined. Therefore the information given below is to some extent arbitrary.

The reactions between organoaluminium compounds and titanium derivatives have been studied in a number of investigations[92–104]. The rate of reaction and the degree of reduction of titanium depend on the nature of the reacting compound: for example, the interaction of triethylaluminium with titanium tetrachloride at a moderate temperature takes place rapidly even in dilute solution[97]. When the concentrations of R_3Al and $TiCl_4$ are approximately equal, then, on the basis of the final products, the reaction between them can be described as follows:

$$AlR_3 + TiCl_4 \rightarrow AlR_2Cl + RTiCl_3 \quad (29)$$
$$\downarrow$$
$$\frac{1}{2}RH + \frac{1}{2}R_{-H} + TiCl_3.$$

The formation of gaseous compounds (methane, ethane, and butane when R = methyl or ethyl) has been attributed to the breakdown of the organotitanium derivative into free radicals with subsequent reactions of the latter[92–96]. A series of alkyl derivatives of titanium have been obtained and investigated†. They are thermally unstable, the most stable being the methyl derivative. Ethyltitanium trichloride decomposes in 24 h at 20 °C.[106]

The interaction of CH_3TiCl_3 with carbon tetrachloride in the presence of metallic mercury takes place via intermediate stages in which free radicals take part[107]. The possibility of the radical polymerisation of vinyl chloride under the influence of organotitanium compounds in combination with carbon tetrachloride has been established[108].

North[109] showed that the polymerisation of styrene under the influence of $RTi(OC_3H_7)_3$ obeys the laws governing free radical reactions. A number of investigators, however, believe that the breakdown of organotitanium compounds takes place without the formation of free radicals and is subject to relations characteristic of bimolecular reactions[98–104]. On the basis of a study of the products of the reaction of $TiCl_4$ with $(C_2H_5)_2AlCl$, de Vries[99] concluded that in this case free radicals are not formed. This conclusion has been confirmed by experimental facts: when the reaction is carried in cumene, dicumenyl (the product of the recombination of the radicals formed when hydrogen is removed from cumene) was not observed; in the reaction in a deuteriated solvent, deuterium was not detected in the gaseous product. On the other hand, the interaction with a deuteriated aluminium alkyl leads to gaseous products which contain an amount of deuterium consistent with the initial content. The formation of such gaseous compounds has been explained[99] from the standpoint of the "self-consistent" bimolecular interaction in which a β-hydrogen atom is transferred from one molecule of the organotitanium compound to another:

$$2\,TiCl_3\text{—}CH_2\text{—}CH_3 \rightarrow 2\,TiCl_3 + C_2H_6 + C_2H_4. \quad (30)$$

De Vries[99] noted that such concepts are particularly useful for the understanding of the stability of methyl derivatives. Shilov and coworkers[102] established that the interaction of $Ti(OR)_4$ with $(C_2H_5)_3Al$ is a two-stage process: initially there is a rapid reaction with evolution of ethane, whose amount corresponds approximately to half of the initial $Ti(OR)_4$ [reaction (31)] and then ethane is formed slowly as a result of reaction (32), which takes place subsequently. When the above reactants interact in deuteriotoluene, deuteriated ethane is not detected in either the first or the second portions of the gas. According to the authors[102], these findings indicate the absence of free radical stages and the formation of gaseous products is a consequence of intramolecular disproportionation. The process can be described as follows:

$$Al(C_2H_5)_3 + Ti(OC_4H_9)_4 \rightarrow {}^1/_2\,C_2H_6 + {}^1/_2C_2H_4^{\ddagger} + \text{(V)} \quad (31)$$

(V) = $(C_2H_5)_2Al(OC_4H_9)_2Ti(OC_4H_9)_2$, with C_4H_9 on the bridging O atoms.

$$V + Al(C_2H_5)_3 \rightarrow \text{(VI)} \rightarrow \text{slow decomposition}. \quad (32)$$

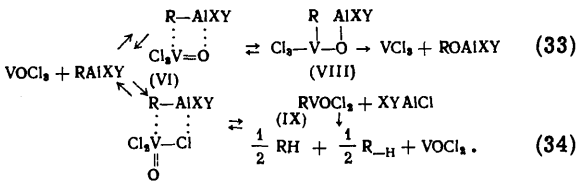
(VI) = $(C_2H_5)_2Al(OC_4H_9)_2Ti(OC_4H_9)_2Al(C_2H_5)_2$, with C_4H_9 on the bridging O atoms and C_2H_5 on Ti.

¶ Systems of the type aluminium alkyl–carbon tetrachloride have been used to initiate the polymerisation of vinyl chloride[85–87].

† See the review of Razuvaev and Latyaeva[105].

‡ The absence of ethylene from the gas evolved is explained by its possible polymerisation.

In the study of the kinetics of the decomposition of CH_3TiCl_3 in carbon tetrachloride Beerman and Bestian[110] established that in this case there is a bimolecular reaction; less than 1% of methyl chloride was detected in the reaction products, which is evidence of only insignificant participation of free radicals in the process. The interaction of organoaluminium compounds with vanadium derivatives, in particular with $VOCl_3$ has been little studied. Petrov showed[111] that the rate of reaction of $VOCl_3$ with $(C_2H_5)_3Al$ is very high; at room temperature the reduction process terminates after less than 2–3 min. Since two possible pathways exist, the process is much more complex than with titanium tetrachloride:



(33)

(34)

The rate of reaction by a particular pathway depends on the relative likelihood of the formation of intermediate complexes (VI) and (VII) and on the stability of compounds (VIII) and (IX).[111] In recent years reliable proof of the formation of organovanadium compounds has been published§. In the study of the mechanism of the breakdown of phenylvanadium oxide dichloride[112] it was established that the decomposition kinetics indicate the occurrence of the following monomolecular reaction:

$$C_6H_5VOCl_2 \rightarrow [C_6H_5^{\cdot} + VOCl_2] \rightarrow C_6H_5{-}C_6H_5. \qquad (35)$$

However, the hypothesis of a radical mechanism for this process is inconsistent with the absence of other reactions characteristic of a highly active phenyl radical (for example the products of the reaction with the cyanodimethylmethyl radical have not been detected, there is no interaction with carbon monoxide, etc.).

Another mechanism has been suggested for the formation of biphenyl[112], which is also consistent with monomolecular decomposition kinetics:

$$2\,C_6H_5VOCl_2 \rightleftarrows (C_6H_5)_2VOCl + VOCl_2, \qquad (36)$$

$$(C_6H_5)_2VOCl \xrightarrow{k} C_6H_5{-}C_6H_5 + VOCl. \qquad (37)$$

The rate of formation of biphenyl is

$$V = k[(C_6H_5)_2VOCl].$$

The equilibrium constant corresponding to reaction (36) is

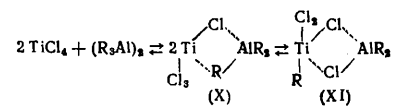
$$K = \frac{[(C_6H_5)_2VOCl]^2}{[(C_6H_5)_2VOCl_2]^2}$$

whence

$$V = k \cdot K^{1/2}[C_6H_5VOCl_2]$$

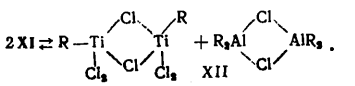
The data quoted demonstrate that the usual procedures in many cases failed to detect the formation of free radicals in the reaction between the components of a Ziegler system in non-polar media. Comparison of the kinetic data for the polymerisation of vinyl chloride under the influence of $(iso\text{-}C_4H_9)_2AlCl{-}Ti(OC_4H_9)_4$ and for the interaction of these components under model conditions established that the fraction of free radical reactions amounts to about 1%.[88] The explanation of the impossibility of isolating the reaction products of free radicals, in particular in experiments with deuteriated solvents, should be based on this finding in the first place. Thus the most sensitive indication of the reactions between the components of the catalyst is the polymerisation itself.

We shall now attempt to represent more fully the reactions which may occur in the catalytic system and the role of the complex-forming agents in the process in those cases where they do not lead to the irreversible consumption of the organometallic compound (the function of the polar monomer should also be determined mainly by its capacity for complex formation). Organoaluminium compounds, which are electron deficient, are known to be capable of forming dimeric species and to participate readily in radical exchange reactions[113–115]. It may be supposed that the first stage of the reaction with a variable-valence metal is the formation of the following association complexes[97]:



(38)

The bimolecular decomposition of compound (XI) leads to the gaseous compounds R–R and $RH(R_{-H})$. Another reaction pathway for the association complex (XI) may be a bimolecular rearrangement of the type¶



(39)

The formation of free radicals may be attributed to the monomolecular decomposition of the organotitanium complex (XII). However, in view of the similarity of the radicals formed, this process takes place mainly by a cryptoradical mechanism with a very small amout of free radicals liberated in the reaction space. The preferential course of the reaction towards the formation of the complexes (XI) or (XII) is associated with the structure of the initial compounds. The specificity of the components of the Ziegler system capable of effecting radical polymerisation consists in the fact that the interaction between them leads to the formation of species tending to undergo homolytic breakdown. In this connection we may note that the stability of organotitanium compounds depends on the nature of R and X (in compounds of the type R_nTiX_{4-n}) and lies in the order indenyl > α-naphthyl > phenyl > *p*-anisyl > > ethynyl > methyl > butyl. On the other hand, the stability increases when the group X has the optimum electronegativity, which is not as high as in the case of fluorine and not as low as in the case of an alkoxy-group[116,117].

The role of complex-forming agents reduces in the first place to the retardation of the subsequent interaction of the metal alkyl and the variable-valence metal having made good their electron deficit; as a result there is a possibility of radical generation in the course of time from rapidly reacting components. The question of the further interaction between the catalyst components in the presence of the complex-forming agent, i.e. the question of the driving forces for this process, remains insufficiently clear. Two pathways may be postulated: in one of them the reaction takes place via non-complex species through the following equilibria:

$$MR_n + K \rightleftarrows MR_n \cdot K,$$
$$MX + K \rightleftarrows MX \cdot K. \qquad (40)$$

§ See the review of Razuvaev and Latyaeva[105].

¶ The absence of an ESR signal in the study of precipitates containing trivalent titanium suggested the existence of dimeric species in titanium halides[100].

i.e. the function of the complex-forming compound is to decrease the concentration of the reacting compounds. This course of the process has been established in the study of the kinetics of the reaction of $(iso\text{-}C_4H_9)_2AlCl-Ti(OC_4H_9)_4$ in the presence of ethyl acetate[118]. Another possibility is the reaction of the complex with displacement of one electron-donor compound by another[119], for example:

$$K\cdot AlR_3 + MX \rightarrow [K \ldots AlR_3 \ldots MX] \rightarrow K + AlR_3\cdot MX\,. \qquad (41)$$

The existence of pentacoordinate aluminium has been unambiguously established recently on the basis of isolated and characterised complexes having the composition

$(C_2H_5)_2AlI\cdot 2\,C_5H_5N$[120] and $(C_2H_5)_3Al\cdot 2,2'$-dipyridyl.[121]

These reactions do not exhaust the role of complex-forming compounds. Association complexes formed by reactions (38) and (39) are also acted upon by the polar reagent, particularly the complexes containing titanium alone [compound (XII)]. There are grounds for the belief that in this case cryptoradical reactions are transformed into true radical reactions. Beerman and Bestian[110] showed that, when CH_3TiCl_3 is decomposed in ether, the process kinetics and the nature of the products formed change. The rate of decomposition increases enormously and the variation with time is consistent with a monomolecular and not a bimolecular reaction. The authors attribute the observed phenomenon to the loosening of the TiR bond under these conditions, which ultimately leads to its homolytic dissociation; the yield of ethane is 28%, while in the absence of ether its amount is negligible.

The decomposition of $C_5H_5VOCl_2$ in the presence of tetrahydrofuran, acetonitrile, and butyl ether is treated by Shilov and coworkers[122] as a free radical process occurring as a result of the increase in the degree of specific solvation of $VOCl_2$ formed relative to the initial compound. A detailed study of the kinetics of the reaction of $(iso\text{-}C_4H_9)_2AlCl$ with $Ti(OC_4H_9)_4$ in the presence of ethyl acetate was made by Budanova and Mazurek[118], who showed that the role of the complex-forming agent at concentrations higher than that of the organoaluminium compound is not restricted solely to the interaction with the initial metal alkyl. In this case there is a change in the order of the reaction with respect to the components of the initiating system, corresponding to a transition from bimolecular to monomolecular breakdown of the intermediate complex of the alkyl derivative of titanium(IV) with generation of free radicals.

The above hypotheses concerning the chemistry of the formation of free radicals and the role of complex-forming compounds are to a large extent tentative. Nevertheless they make it possible to understand the causes of the difference between ionic-coordination polymerisation and the polymerisation of polar monomers. The latter gives rise not to the final reaction product MR_n-MX_m but to unstable intermediate compounds formed in the course of this reaction.

At the present time the hypothesis that in ionic-coordination polymerisation the propagation steps are preceded by the coordination of the double bond of the monomer to the unfilled orbitals of the variable valence metal has been widely adopted. As shown for titanium tetrachloride, in the case of polar monomers where the heteroatom is in the β-position with respect to the double bond the preferred coordination site is located at the polar groups[123]. To what extent such concepts are valid also for trivalent titanium (or other metals in a lower valence state) remains obscure at present. Therefore we should note that the literature data quoted, indicating the occurrence of radical polymerisation of polar monomers using Ziegler catalysts, nevertheless do not exclude the possibility that in special cases ionic-coordination polymerisation of this class of monomers can also take place.

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During the preparation of the manuscript for the press new literature data were published which can usefully supplement the corresponding sections of the review.

1. The problem of whether the conversion of organic peroxoboron derivatives into alkoxyboron derivatives takes place by an intramolecular or intermolecular mechanism[22-27] was examined in detail by Mirviss[124].

2. It is interesting to compare the postulates put forward by Hansen[34] with the results of Bednarec et al.[125], who investigated the polymerisation of vinyl chloride under the influence of $(C_4H_9)_3B-O_2$ and showed that the overall activation energy for the polymerisation reaction varies from 11 to 6.5 kcal mole^{-1} between 0° and −30°C and between −40° and −70°C respectively. According to Bednarec et al.[125], the observed effect is evidence for the coexistence under such conditions of several types of initiating systems, which leads to the variation of the activation energy for the initiating reaction and correspondingly the overall energy of the process.

3. It has been established[126] that the interaction of $AlPh_3$ with benzophenone under model conditions is accompanied by the formation of free radicals. This is associated with the ease of homolysis of the adduct $(Ph_3COAlPh_2)_2$ and not with one-electron transfer, postulated[17] for organocadmium compounds.

4. We believe it to be appropriate also to quote data for a very interesting system obtained by combining an aluminium alkyl with azobis(isobutyronitrile)[127]† and to compare the results with other data[42-48]. It has been shown[127] that the systems investigated [R_3Al–azobis(isobutyronitrile) or R_2AlCl–azobis(isobutyronitrile)] are capable of initiating the radical polymerisation of vinyl chloride and styrene (but not methyl methacrylate) at a lower temperature than is the case in the breakdown of the azobis(isobutyronitrile) itself. The nature of the radicals identified by electron spin resonance (ethyl and cyanodimethylmethyl) indicates the participation of both components of the system in the generation of free radicals. The authors[127] attribute their findings to the formation of the complex R_3Al–azobis(isobutyronitrile) (via the nitrile group of the latter) in which radical breakdown is facilitated.

5. The data quoted in Refs. 58 and 59 and 128 are supplemented by the findings that the polymerisation of methyl methacrylate by the catalytic system $(C_2H_5)_3Al-Ti(OC_4H_9)_4$ is also regarded as a catalytic process.

6. In the course of further development of their studies[81,82], Yamazaki and coworkers[129] investigated the polymerisation of deuteriated vinyl chloride by the system $(C_2H_5)AlCl_2-Ti(OR)_4$ and established the presence of terminal alkyl groups. This suggested that the initiation process may have a radical mechanism. However, the authors believe that the nature of the propagation stage is still obscure.

7. The work of Ulbricht et al.[130], who concluded that the polymerisation of vinyl chloride under the action of the

† This is the first piece of evidence indicating the possibility of influencing catalytically the rate of decomposition of azobis(isobutyronitrile).

system $TiCl_4$–Et_2AlOEt–dioxan (on the basis of their kinetics and the measured copolymerisation constants for vinyl chloride–styrene), is related to the investigation in Refs. 80 and 88.

8. The concepts put forward in Refs. 82, 90, and 91 may ber supplemented by the results of Yamazaki and Aridomi[131], who showed that, depending on the composition of the catalyst $TiCl_x(OC_4H_9)_{4-x}$–$AlCl_y(C_2H_5)_{3-y}$ (where x = 0–4 and y = 0–2), the vinyl chloride–propene copolymerisation constants may correspond to either a radical or an ionic-coordination process. Yamazaki and Aridomi[131] suggest that this finding should be attributed to the possibility of the polymerisation of vinyl chloride itself by one or other mechanism.

9. In agreement with the results of Beerman and Bestian[110], it has been shown[132] that the breakdown of CH_3TiCl_3 in tetrahydrofuran is homolytic. The formation of the CH_3 radical has been confirmed by the presence in the reaction mixture of CH_3D when the reaction is carried out in deuteriotoluene.

10. It is interesting to compare the effect of complex-forming additives on the type of decomposition of variable-valence organometallic compounds, established under model conditions[110,122,132], with the findings for the polymerisation process. Thus it has been shown[133] that in the copolymerisation of ethylene with vinyl chloride by the catalytic system Et_2AlCl–$Ti(OR)_4$ the addition of electron donors (tetrahydrofuran, pyridine, ethyl ether, diethylamine) leads to the formation of copolymers, the structure of which fully corresponds to that obtained under the conditions of a radical process[134].

11. A fundamentally new procedure for the ionic-coordination polymerisation of polar monomers by Ziegler catalysts was proposed by Giannini et al.[135] Its essential feature is that one uses in the reaction either monomers with sterically hindered (with respect to the reactions with the catalyst) functional groups or monomers with reduced electron-donor capacity (this is achieved by preliminary complex formation with an organometallic compound or by using monomers containing O–Si bonds).

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Institute of Macromolecular
Compounds, Leningrad

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β-Ketovinylation

M.I.Rybinskaya, A.N.Nesmeyanov, and N.K.Kochetkov

The review deals with the methods of introduction into the molecule of the group RCOCR′=CR″, which has come to be called the β-ketovinylation reaction. It has been shown that the principal starting materials for these reactions are certain β-substituted vinyl ketones, which have surpassed all other activated ethylene compounds in their importance for synthetic organic chemistry. A systematic description of literature data has been given in accordance with methods for *C*-, *N*-, *O*-, *S*-, *P*-, *Hal*-, *Fe*-, and *Co*-ketovinylation. This made it possible to make generalisations and recommendations concerning the choice of the ketovinylating agent in particular cases. The possible mechanism of β-ketovinylation is discussed, particular attention being devoted to kinetic and stereochemical data. The bibliography comprises 300 references.

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I. INTRODUCTION

Cyanoethylation, the Michael condensation, and other reactions based on the capacity of the activated double bond to combine with nucleophilic reagents have played a considerable role in the development of synthetic organic chemistry. Among these reaction types, one of the most important is the β-ketovinylation reactions, despite the fact that the method hardly began to be developed until the 1950's. It is noteworthy that the main advances in this field have been achieved by Soviet chemists.

Ketovinylation reactions involve the introduction of a preformed RCOCR′=CR″ group into the molecule[1]. These reactions have led to a new synthesis of αβ-unsaturated ketones, and a very wide variety of β-substituted vinyl ketones, in which the RCOCR′=CR″ group is linked with the atoms of various elements, have become available. Among the compounds obtained particular mention should be made of the σ complexes of the RCOCR′=CR″ group with the atoms of transition metals such as iron and cobalt. The availability of these derivatives extends the possibilities of the synthesis of organometallic compounds, since the RCOCR′=CR″ fragment is bifunctional. The high activity of the carbonyl group in β-substituted vinyl ketones had led in turn to the development of methods for the preparation of many heterocycles. The extensive studies of the properties of β-substituted vinyl ketones have shown that these compounds are not only of interest in connection with synthesis but can serve as convenient models for the elucidation of certain theoretical questions associated with the mechanisms of nucleophilic substitution and addition to an activated double bond.

The RCOCR′=CR″ group may be introduced into the molecule in two ways. 1. By nucleophilic substitution of X in compounds of the type RCOCR′=CR″X:

$$RCOCR'=CR''X + Y^- \rightarrow RCOCR'=CR''Y + X^-,$$

where X = Hal, OR, OH, NR_2, $\overset{+}{N}R_3$, etc. 2. By the addition of nucleophilic agents to the triple bond of ethynyl ketones

$$RCOC{\equiv}CR' + Y^- \xrightarrow{H^+} RCOCH{=}CR'Y.$$

The first method is used more often, and its development has been particularly intense after general methods for the synthesis of β-chlorovinyl ketones have become available[2-4].

Despite the large number of studies on the chemistry of β-substituted vinyl ketones, a systematic account of β-ketovinylation methods has not been published so far. There are several reviews in the literature dealing with syntheses on the basis of β-chlorovinyl ketones[1,5-8] or their derivatives—β-ketoacetals[9]. In 1961 Kochetkov and coworkers published a review on the *C*-ketovinylation of β-dicarbonyl compounds[10]. In the present review the authors attempted to give a systematic account for the first time of other methods of β-ketovinylation, including *C*-, *N*-, *O*-, *S*-, *P*-, *Hal*-, *Fe*, and *Co*-ketovinylation. Examination of the literature data in this context permits certain generalisations and recommendations for the choice of the method of synthesis of αβ-unsaturated ketones in particular cases. The review includes literature data up to 1st January 1968.

II. METHODS OF β-KETOVINYLATION

1. *C*-Ketovinylation

Among other β-ketovinylation reactions, the methods for the formation of a carbon–ketovinyl bond (*C*-ketovinylation) occupy one of the most important places. The development of these methods not only led to the ready availability of all possible αβ-unsaturated aliphatic, aromatic, and heterocyclic ketones, but has also permitted the synthesis of certain cyclic compounds and also stable organic anions and polymers with a conjugated system of double bonds.

It would appear that carbanions should undergo ketovinylation most readily. However, with powerful nucleophilic reagents such as the carbanions of the organometallic compounds of Group I elements and magnesium, complications arise due to the additional possibility of reaction at the carbonyl group. It is noteworthy that numerous investigations of the reactions of αβ-unsaturated ketones with these nucleophilic reagents have not so far provided a definite answer to the question why 1,2- and 1,4-addition takes place. However, with β-substituted vinyl ketones it is possible to follow the effect of the nature of the β-substituent on the mode of attack on the carbanions. It has been found that β-chlorovinyl ketones cannot be used for the ketovinylation of aliphatic and aromatic carbanions. In this case the carbonyl group is mainly attacked and the reaction yields carbinols. It is noteworthy that the rearrangement of such carbinols in an acid medium is used for the preparation of αβ-unsaturated aldehydes of type (I)[11-16]:

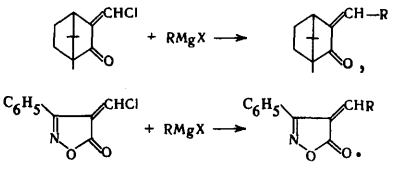
$$RCOCH{=}CHCl + R'M \rightarrow \overline{O}{-}CRR'{-}CH{=}CHCl \xrightarrow{H_3O^+} \underset{(I)}{RR'C{-}CH{=}CH{-}O}.$$

β-Chloroacrolein[17] and its polyhalogeno-derivatives[18-20] react similarly and this was used by Skoldinov et al.[17] in the synthesis of the *cis*- and *trans*-isomers of β-chlorovinyl methyl ketone (see p. 450).

However, in reactions with organometallic compounds having a less polarised metal–carbon bond, such as cadmium derivatives, the successful use of β-chlorovinyl ketones is also possible[21,22]:

$$RCOCH{=}CHCl + \overset{-\delta}{R'}{-}\overset{+\delta}{Cd}{-}R' \rightarrow R{-}\underset{\underset{O}{|}}{C}{-}CH{=}CHR'.$$

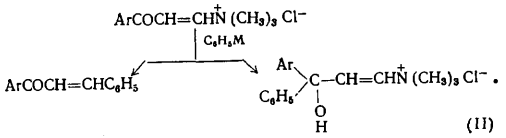
Furthermore, normal ketovinylation of RLi and RMgX by β-chlorovinyl ketones is possible in those cases where the approach to the carbonyl group is sterically hindered (for example, when the carbonyl group is in a ring)[22-25]:



The replacement of the chlorine atom in substituted β-chlorovinyl ketones by a phenoxy-group favours the formation of ketovinylation products and their derivatives, but the yields are only 20–40%:[26]

$$CH_3COCH{=}CHOC_6H_5 \xrightarrow{CH_3MgBr} [CH_3COCH{=}CHCH_3] \xrightarrow{CH_3MgBr} \rightarrow CH_3{-}\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH{=}CH{-}CH_3 \rightarrow CH_2{=}\underset{\underset{CH_3}{|}}{C}{-}CH{=}CH{-}CH_3.$$

Vinyl ketones containing a powerful electron-acceptor group such as the quaternary ammonium group in the β-position relative to the carbonyl group react with C_6H_5Li to form a mixture of *C*-ketovinylation and 1,2-addition [compounds (II)] products in almost equal amounts†. When C_6H_5MgBr is used, the yield of *C*-ketovinylation products is much higher:[27]



(II)

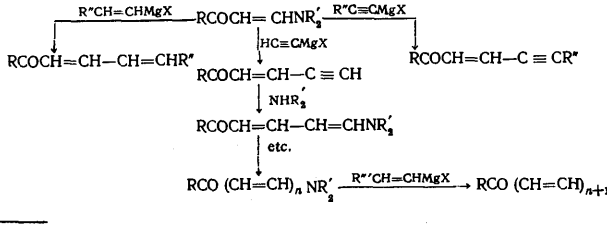
Thus, despite the pronounced electron-acceptor properties of the quaternary ammonium group, which should apparently intensify the electrophilicity of the carbonyl carbon atom, *C*-ketovinylation products are formed in appreciable amounts. This is probably because the $\overset{+}{N}(CH_3)_3$ group attracts electrons by an inductive effect, so that the positive charge appears also at the carbon atoms of the double bonds. In this connection it is interesting to note that the sulphonyl group, which exhibits a powerful I-effect, is also substituted on interaction of organomagnesium compounds with phenyl β-phenylsulphonylvinyl ketone[29]:

$$C_6H_5COCH{=}CHSO_2C_6H_5 + C_6H_5MgX \rightarrow C_6H_5COCH{=}CHC_6H_5.$$

On the other hand, in most cases β-dialkylaminovinyl ketones[30,31], which are less reactive than β-chlorovinyl ketones, are convenient reagents for the ketovinylation of RLi, RNa, and RMgX:

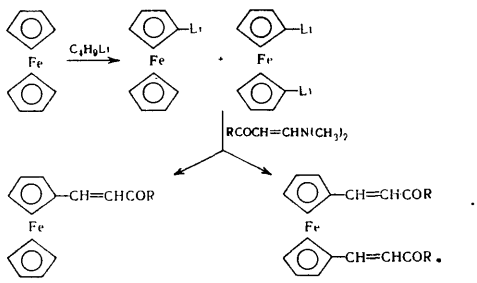
$$RCOCH{=}CHN(CH_3)_2 + R'Li \rightarrow RCOCH{=}CHR'.$$

This was shown experimentally by Benary for the first time[30] and later Normant and coworkers[31] developed an elegant method for the synthesis of conjugated keto-polyenes and keto-enynes:

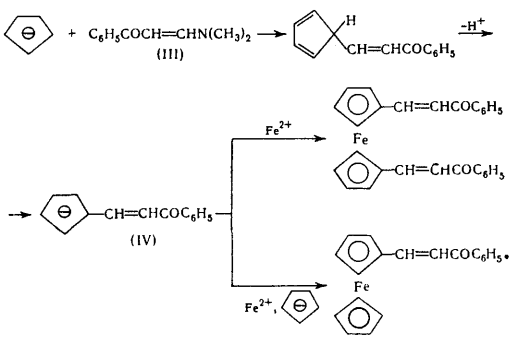


† It has been found[28] that the salts (II) may be used to synthesise the hitherto unknown quaternary ammonium salts containing the indenyl group.

Nesmeyanov and coworkers[32] used this method for the preparation of mono- and di-ketovinylated ferrocenes by the following procedure:



The same compounds were obtained[33] by the ketovinylation of the cyclopentadienide ion with β-dimethylaminovinyl phenyl ketone (III) followed by treatment of the reaction mixture with anhydrous iron(II) chloride:

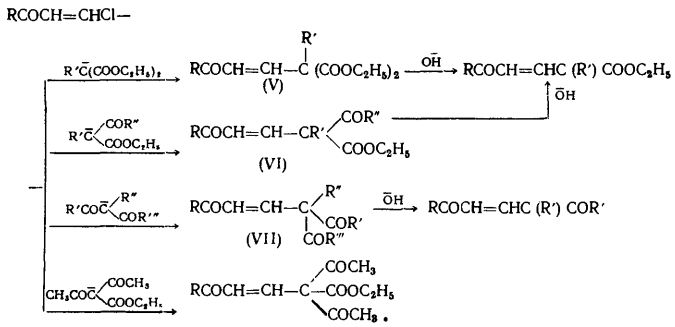


The yield of the ion(IV), which amounted to about 40 mole %, may be estimated from the amounts of mono- and di-ketovinylated ferrocenes produced. Thus the ketovinylation method developed may be used for the synthesis of αβ-unsaturated ketones of the ferrocene series.

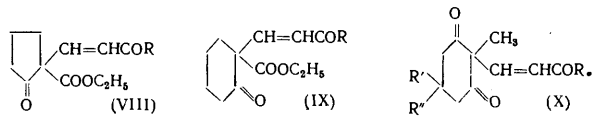
Ketovinylation reactions have assumed particular importance in the synthesis of heteroannular dicarbonylvinyl derivatives of ferrocenes. The very possibility of synthesising such derivatives was discovered solely owing to the development of these methods.

It is interesting to note that β-chlorovinyl ketones can also be used in the reaction with the cyclopentadienide ion‡, but in this case the process does not stop at the first stage and polyketovinylation products are formed[34].

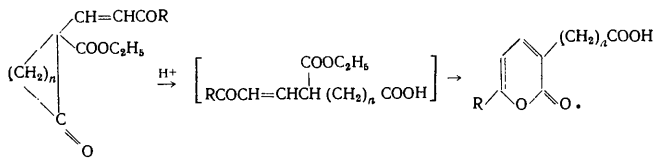
The ketovinylation of carbon-containing ambident anions takes place very readily. Such ions include in the first place the anions of β-dicarbonyl compounds, ketones, nitro-compounds, etc. The reactions with β-dicarbonyl compounds (β-diketones, β-keto-esters, malonic ester, and their derivatives) have been investigated in detail by Kochetkov and coworkers[10]. β-Chlorovinyl ketones were used as ketovinylating agents. It was found that β-dicarbonyl compounds are normally ketovinylated only when they contain one labile hydrogen atom[35-39]:



Methods for the synthesis of unsaturated keto-acids and diketones have been developed on the basis of these reactions. For example, under the action of bases, compounds of type (V) eliminate the ethoxycarbonyl group and are converted into δ-keto-βγ-unsaturated acids[40] and compounds of type (VI) readily undergo the ketonic decomposition[41]. The same reactions were observed with the triketones (VII).[37] Cyclic β-keto-acids[42] and β-diketones[37,43] are of course ketovinylated without complications, compounds of types (VIII)-(X) being formed:



It is noteworthy that the rearrangement of compounds (VIII) and (IX) and analogous compounds under the action of acids has been proposed as a method for the synthesis of α-pyrones[44,45]:

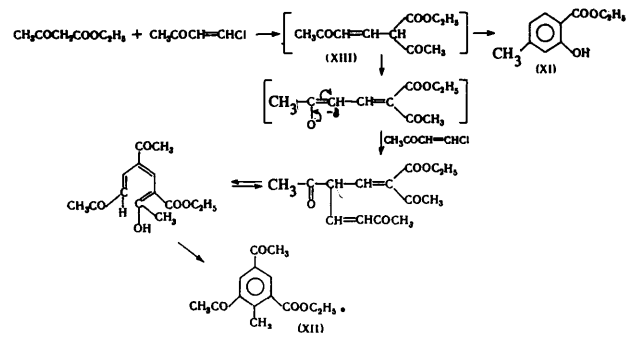


It has been found that the yields of ketovinylation products vary appreciably depending on the nature of the β-dicarbonylcompound: esters of alkylmalonic and α-substituted acetoacetic acids reacts with higher yields than β-diketones, while the diacetylacetic ester does not react at all[10]. Probably the decrease of the yields of ketovinylation products in this series may be attributed to the increase of the stability and hence the decrease of the nucleophilicity of the attacking mesomeric anions formed from the corresponding carbonyl compounds.

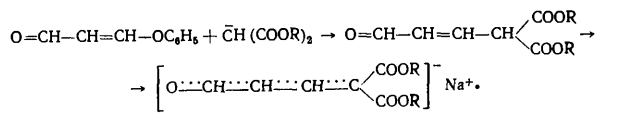
In contrast to the single-proton β-dicarbonyl compounds, the two-proton (with two labile hydrogen atoms) malonic and acetoacetic esters react with β-chlorovinyl ketones under analogous conditions to form a complex mixture of products. For example, when β-chlorovinyl methyl ketone reacts with acetoacetic ester in the presence of potassium carbonate, two compounds are formed: ethyl 4-methylsalicylate (XI) and the ester of 3,5-diacetyl-2-methylbenzoic acid (XII).[46,47] The amounts of the two products, (XI) and (XII), in the mixture depend on the ratio of the starting

‡ In contrast to aliphatic and aromatic ions, the cyclopentadienide ion is not a very powerful base, becoming readily polarised, and therefore it reacts with β-chlorovinyl ketones via the β-carbon atom of the ethylene bond (see page 446).

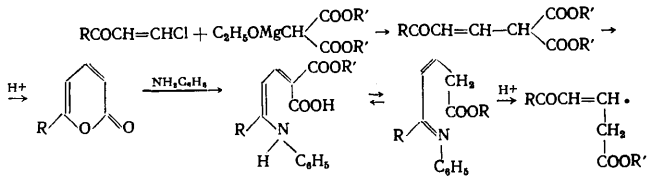
materials. The formation of compounds (XI) and (XII) may be accounted for by the following mechanism:



Under the reaction conditions the mono-ketovinylation product (XIII) undergoes further cyclisation to compound (XI). However, since the intermediate (XIII) is a stronger acid than the initial acetoacetic ester, it readily produces an anion which is capable of being ketovinylated. In turn compound (XII) is formed as a result of the cyclisation of the ketovinylation product. It is interesting to note[48] that, when hydroxymethylene ketones, the double bond of which is less electrophilic than in β-chlorovinyl ketones, are employed in this reaction, the process stops at the mono-ketovinylation stage[48] and only 4-methylsalicylic acid (XI) was isolated. Of course, the capacity for subsequent ketovinylation depends not only on the electrophilicity of the β-carbon atom of the ketovinylating agent but also on the stability of the anion formed as the result of mono-ketovinylation. Thus, in the interaction of sodiomalonic ester with β-phenoxyacrolein[49], the product is the stable anion of an acid with a strength approximately equal to that of acetic acid ($K_a = 1.4 \times 10^{-5}$). The nucleophilicity of this anion proved to be too low for it to react again with β-phenoxyacrolein and the reaction stops in the first stage:

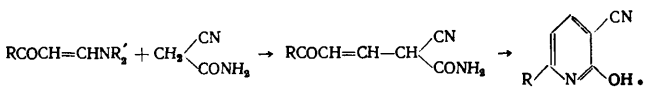


In order to avoid complications associated with successive ketovinylation, Kochetkov and Kudryashov[50] employed the ethoxymagnesium derivative of malonic ester in benzene in the reaction with β-chlorovinyl ketones. In this case the reaction takes place fairly smoothly and α-ethoxycarbonyl-δ-keto-βγ-unsaturated acids are formed in high yields. It proved possible to convert these acids into α-pyrones and further into the vinylogues of acylacetic esters[51]:



It is noteworthy that under these conditions the reaction with acetoacetic ester did not yield satisfactory results[50].

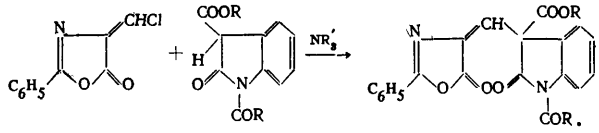
The reaction of β-dialkylaminovinyl ketones with cyanoacetamide can also be regarded as monoketovinylation with subsequent cyclisation—the nitriles of 6-alkyl-2-hydroxynicotinic acids were obtained[52]:



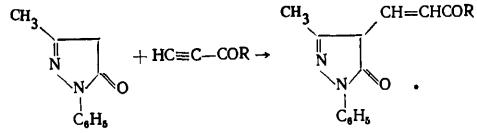
The reaction of ethyl β-diethylaminovinyl ketone with cyclic ketones was achieved by Abe[53].

Ketovinylation with β-hydroxyvinyl ketones[54], β-methoxyvinyl ketones[55] or their derivatives, and also acetals of β-keto-aldehydes[56] requires the use of catalysts, for example piperidinium acetate.

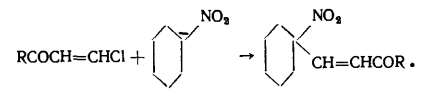
Behringer and coworkers[22,25] used tertiary amines as condensing agents in the reaction of heterocyclic analogues of β-chlorovinyl ketones with various compounds containing a methylene group with labile hydrogen atoms:



Probably quaternary carbonylvinyl ammonium salts, which are very powerful ketovinylating agents, are formed in this case as intermediates. However, the explicit use of the open-chain quaternary salts $RCOCH{=}CH\overset{+}{N}(CH_3)_3Cl^-$ in the ketovinylation of the anions of the malonic and acetoacetic esters did not yield satisfactory results[50]. Ethynyl ketones have also been used for the ketovinylation of heterocyclic compounds[57]:

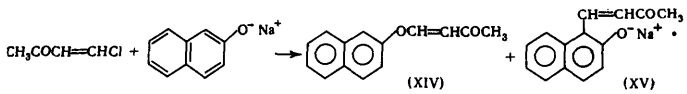


The possibility in principle of the ketovinylation of nitro-compounds with one labile hydrogen atom in the α-position has been demonstrated for 2-nitropropane[58] and nitrocyclohexane[59,60]. The choice of these nitro-compounds was again dictated by the possibility of further ketovinylation in the presence of two labile α-hydrogen atoms:



Unfortunately the yields of ketovinylation products in these cases are low.

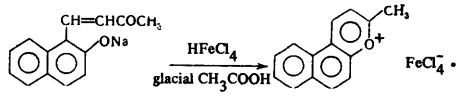
Yet another example of the ketovinylation of an ambident ion is the reaction of sodium β-naphthoxide with β-chlorovinyl ketones. The authors of the present review showed[61] that their reaction yields both series of derivatives§, the ratio of the products of *C*- and *O*-ketovinylation depending markedly on the solvent. In an aqueous alkaline medium the main product is methyl β-(2-naphthoxy)vinyl ketone (XIV) (63%) and only 10% of sodium 1-(β-acetylvinyl)-2-naphthoxide (XV) is formed, while in dioxan the main product is compound (XV) (50.5%) and the yield of compound (XIV) is only 19%:



Probably the effect of the solvent on the mode of ketovinylation is due to the fact that in an aqueous alkaline medium the oxygen of the β-naphthoxide is mainly attacked, while in the reaction in dioxan the oxygen atom is blocked by the cation, since here only the closely linked ion pairs $\beta\text{-}C_{10}H_7O^-Na^+$ exist. For this reason, the *C*-ketovinylation product is formed preferentially in dioxan. The structure

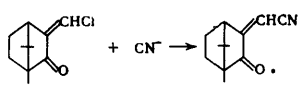
§ We may note that only the *O*-derivative is formed in the ketovinylation of the phenoxide anion[61,62].

of compound (XV) was demonstrated by its ready ring closure to form a salt of 2-methylnaphthopyrylium:



It is noteworthy that the same salt was obtained[61] by the direct reaction of β-chlorovinyl methyl ketone with β-naphthol (see p. 438).

The importance of the correct choice fo the ketovinylating agent is well illustrated by the cyanide ion as an example. The ketovinylation of the cyanide ion with chloromethylenecamphor was achieved for the first time by Bishop et al.[63] as early as the end of the previous century:



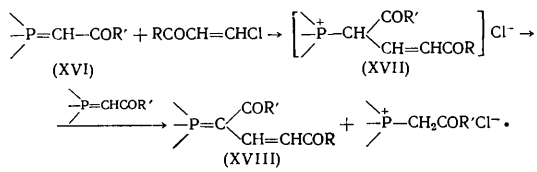
However, the reaction of open-chain β-chlorovinyl ketones with cyanide ions proved to be quite impossible. In his study of this reaction using β-chlorovinyl phenyl ketone in non-polar media, Pannizzi[64] isolated the starting material. The attempts to ketovinylate alkali metal cyanides in polar solvents (water and alcohol) also proved to be unsuccessful. In this case the reaction takes place extremely vigorously and the initial β-chlorovinyl ketones vanish completely, but dark coloured resins are formed instead of the expected products. The ketovinylation of copper cyanide also failed. It is noteworthy that the attempt to replace the chlorine atoms in β,β-dichlorovinyl ketones by CN groups was also unsuccessful[65].

The ketovinylation of the cyanide ion was achieved only when quaternary carbonylvinylammonium salts were employed[66]:

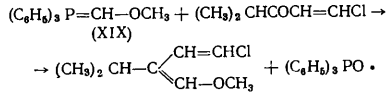
$$RCOCH{=}CH\overset{+}{N}(CH_3)_3 + CN^- \rightarrow RCOCH{=}CHCN + N(CH_3)_3.$$

The ready solubility in water of the initial salts and the sparing solubility of the resulting β-cyanovinyl ketones play a significant role in this synthesis. The successful ketovinylation of the cyanide ion lead to the development of a new synthesis of β-aroylacrylic acids and their amides[67].

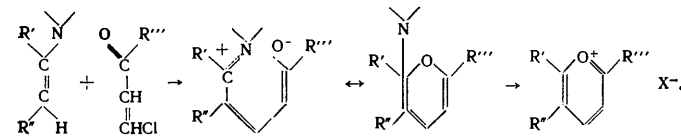
Phosphorylides, which may be regarded as dipolar ions, react in different ways with β-chlorovinyl ketones, depending on the structure of the phosphorylide. Stabilised phosphorylides of type (XVI) probably form intermediate phosphonium salts (XVII), which react further with the second molecule of the phosphorylide and are converted into a ketovinylated phosphorylide (XVIII):



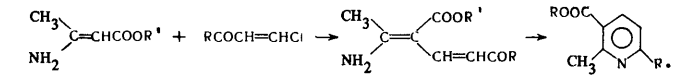
On the other hand, methoxymethylenetriphenylphosphorane (XIX) undergoes the normal Wittig reaction[68]:



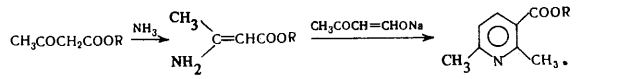
Ketovinylation can be achieved also with neutral unsaturated molecules having a multiple bond with enhanced electron density. Thus it has been found[69] that enamines react very readily with β-chlorovinyl ketones, dipolar ions, from which pyrylium salts were subsequently obtained, being formed as intermediates:



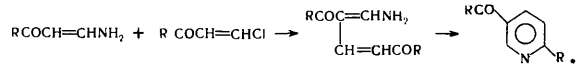
Probably the reaction of β-chlorovinyl ketones with methyl β-aminocrotonate is also accompanied by initial *C*-ketovinylation[70]. A method for the synthesis of 2,6-dialkyl-3-ethoxycarbonylpyridines was developed on the basis of this reaction:



β-Dicarbonyl compounds[70,71] in an excess of ammonia may be used in the reaction instead of the actual enamines. For example, Rabe[71] obtained 3-ethoxycarbonyl-2,6-dimethylpyridine by the reaction

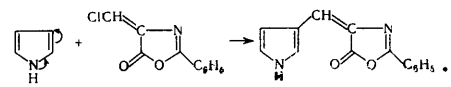


β-Aminovinyl ketones are also capable of undergoing *C*-ketovinylation. A method for the synthesis of 2,6-dialkyl-3-acylpyridines was developed on the basis of this reaction[72,73]:

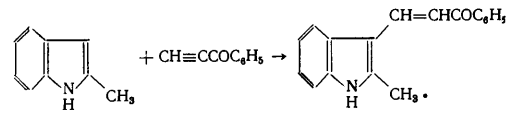


The method is convenient for the synthesis of fusaric acid[74,75].

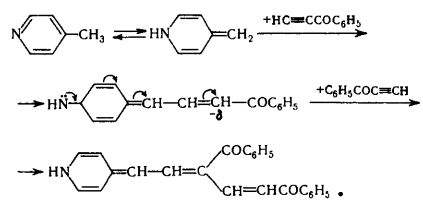
The reaction of β-chlorovinyl ketones and related compounds with pyrroles and indoles may be regarded as a special case of ketovinylation of enamines[22,76]:



Ethynyl ketones have also been used for this purpose[77]:

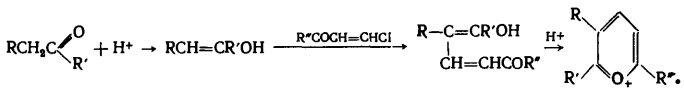


γ-Picolines react with ethynyl ketones like enamines with a longer conjugation chain; the reaction does not stop at the first stage and coloured diketovinylated products are formed[77] (see the section dealing with the ketovinylation of β-dicarbonyl compounds having two labile methylene hydrogen atoms):



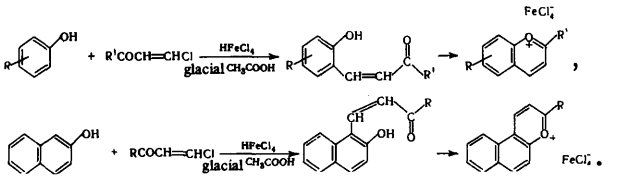
The ketovinylation of the system $\rangle C{=}C{-}OH$ was studied in many instances. The reaction of ketones with hydroxymethylene ketones in an acid medium was discovered[78] as

early as 1924 but was ignored for many years and its systematic study began only recently. It was found that under these conditions not only hydroxymethylene ketones [79-82] but also β-chlorovinyl ketones [83] can enter into the reaction. As a result, a general method has been developed for the synthesis of pyrylium salts:

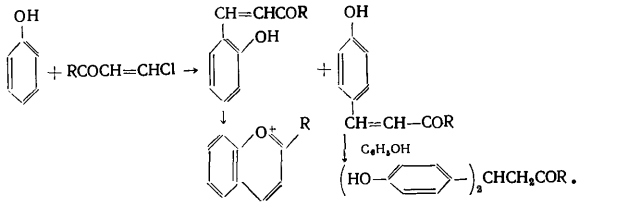


It is interesting to note that, according to the data of Zakharkin and Sorokina [84-87], in the case of ββ-dichloroacrolein the carbonyl group is attacked.

β-Chlorovinylketones react very readily with phenols and β-naphthol in the presence of a condensing agent—a mixture of iron(III) chloride and hydrochloric acid. On the basis of this reaction, Nesmeyanov, Kochetkov, and Rybinskaya developed a preparative method for the synthesis of benzopyrylium [88,89], flavylium [89], and naphthopyrylium salts [88,90]:



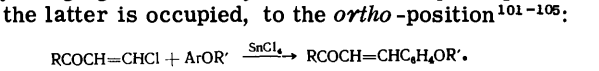
In the case of phenols with a free *para*-position, other products are formed from the phenols ketovinylated in the *para*-position together with the benzopyrylium salts. The former combine with a further phenol molecule at the double bond under the reaction conditions [91]:



A strongly activated system, such as phloroglucinol reacts with β-chlorovinyl ketones even in the absence of catalysts. This led to the development of a very simple synthesis of the methyl ester of a natural anthocyanidine—hesperidin chloride [89]. The reaction with pyrogallol requires heat [22].

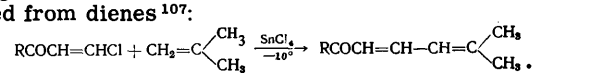
The methods for the synthesis of salts with a pyrylium ring using β-hydroxyvinyl ketones (β-diketones capable of enolisation) were investigated in greater detail [92-100].

Phenolic ethers can also be made to undergo the ketovinylation reaction and best results are achieved when tin(IV) chloride is used as the catalyst. The attack of the ketovinylating agent is mainly directed to the *para*-position and, if the latter is occupied, to the *ortho*-position [101-105]:

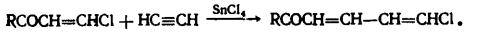


It is noteworthy that thiophen reacts under these conditions like phenolic ethers [106].

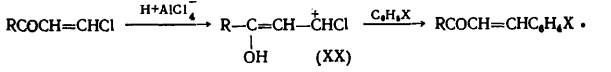
Tin(IV) proved to be an extremely active catalyst also in the condensation of β-chlorovinyl ketones with olefins having alkyl substituents at the double bond. This reaction takes place so easily with isobutene that fairly pronounced cooling (−10°C) is required. The reaction yields ketones derived from dienes [107]:



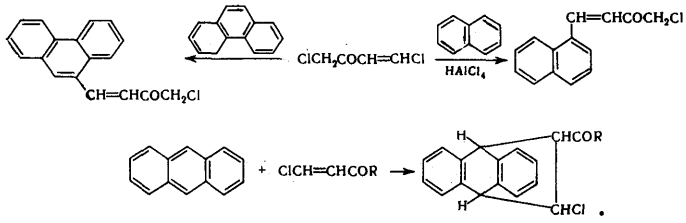
In this connection it is noteworthy that, in the presence of tin(IV) chloride, it even proved possible to achieve the reaction of acetylene with β-chlorovinyl ketones [107]. This reaction is interesting because it permits the preparation of the vinylogues of β-chlorovinyl ketones:



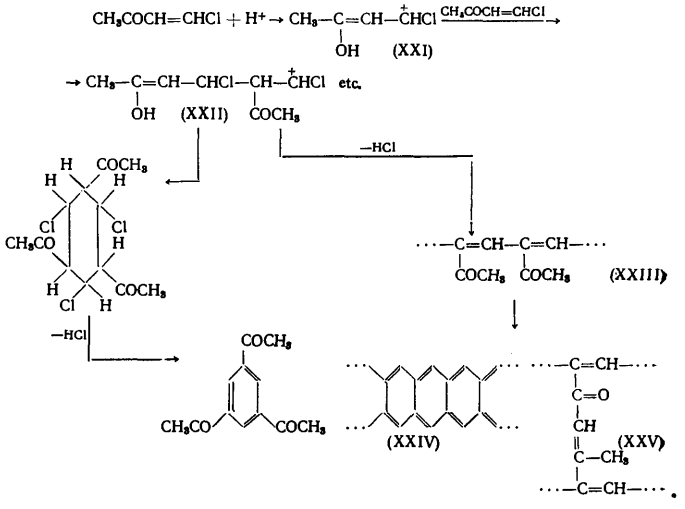
However, with very weak nucleophilic agents such as benzene and its homologues ketovinylation does not occur even in the presence of Friedel–Crafts catalysts. Probably this is because the double bond in β-chlorovinyl ketones, even when it is additionally polarised by the action of the catalyst, is still insufficiently electrophilic. In order to increase the positive charge at the β-carbon atom of the double bond, a stream of moist hydrogen chloride was passed into the reaction mixture containing aluminium chloride. In this case the reaction took place extremely readily and even chlorobenzene could be made to react [108]. It is suggested that the active species in this reaction is the intermediate carbonium ion (XX):



Naphthalene and phenanthrene [34] reacted readily under the same conditions and only in the case of anthracene [109] were diene condensation products obtained instead of the ketovinylated derivatives:



The unusual polyketovinylation or, more correctly, polycondensation of β-chlorovinyl methyl ketone, which is accelerated in the presence of acid reagents, should also be classified as a *C*-ketovinylation reaction. Depending on the reaction conditions, a cyclic trimer (triacetylbenzene) or a polymer with a conjugated system of bonds can then form [34,110]. The active species in this process is probably the carbonium ion (XXI). This ion attacks the next molecule with formation of a new carbonium ion (XXII), etc.:



Condensation in solution yields a cyclisation product, while in the absence of solvent a polymer is formed, which, as a result of spontaneous dehydrochlorination, yields the polyene (XXIII). The polymer (XXIII) changes slowly on heating in a vacuum with evolution of water, which is probably due to the crotonic condensation of the acetyl group in the chain or between the chains. As a result, the polymer may contain units consisting of condensed aromatic rings (XXIV) and units of type (XXV). According to infrared spectroscopic data, fragments of type (XXIV) probably predominate in the polymer. The study of electrical and magnetic properties showed[111,112] that the polymers may be regarded as "organic" semiconductors. Their ability to catalyse certain reactions, in particular the oxidation of toluene to benzaldehyde and benzoic acid[111], proved to be specially interesting.

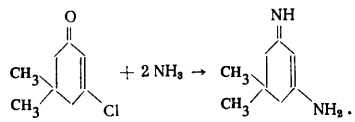
In conclusion it should be noted that the formation of triacetylbenzene was observed also in the polycondensation of other compounds of the type $CH_3COCH=CHX$, for example with X = OH, OCH_3, OCOR, etc. It was found that here too polycondensation is facilitated by acids[113-115].

2. *N*-Ketovinylation

Ammonia and primary, secondary, and tertiary amines readily undergo ketovinylation. The principal ketovinylating agents in these processes are β-chlorovinyl ketones[116-119]:

$$RCOCH=CHCl + NH_3 \rightarrow RCOCH=CHNH_2.$$

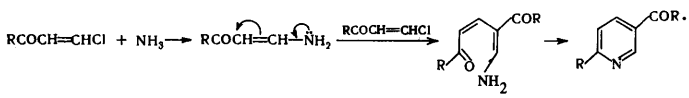
Information about this reaction appeared for the first time in the patent literature[120-121], where it was suggested that β-aminovinyl ketones be used as antidetonators and as intermediates for the synthesis of dyes and insecticides. In some cases two molecules of ammonia enter into the reaction simultaneously (at 100°C), which results in the formation of imines derived from β-aminovinyl ketones[122]:



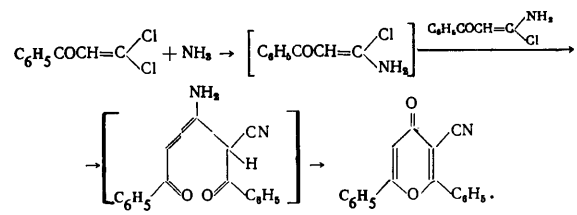
Since ammonia and amines are fairly powerful nucleophilic reagents, hydroxymethylene ketones and their enolates and ethers may take part in *N*-ketovinylation[123]. β-Aminoacrolein was also obtained by the treatment of β-methoxyacrolein with ammonia[124]. Ethynyl ketones were used successfully in this reaction[125]:

$$RCOC\equiv CH + NH_3 \rightarrow RCOCH=CHNH_2.$$

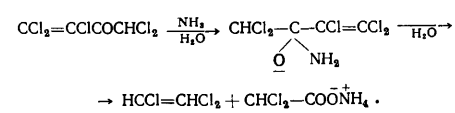
When aqueous ammonia reacts with an excess of β-chlorovinyl ketones[126-128] and ethynyl ketones[129], 2-alkyl-5-acylpyridines are formed. Possibly the intermediates in this reaction are β-aminovinyl ketones, which cyclise with the excess of the initial reagent to form the corresponding pyridine derivative[72,126,129]:



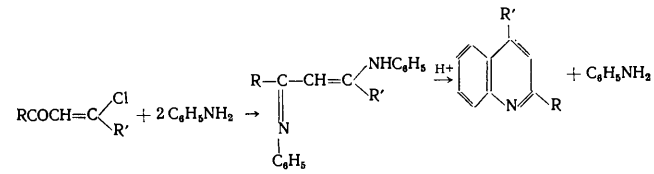
A similar mechanism may be proposed for the reaction of ammonia with ββ-dichlorovinyl phenyl ketone[8], which led to the formation of the nitrile of 2,6-diphenyl-γ-pyrone-3-carboxylic acid:



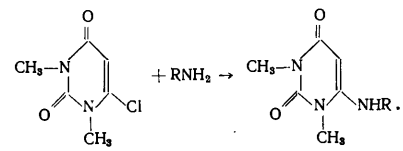
However, the situation changes fundamentally when polychloro-substituted αβ-unsaturated ketones are employed. Roedig and Maier[130] found that this results in the fission of the initial compound into trichloroethylene and a carboxylic acid salt. Probably in this case nucleophilic attack is directed to the carbonyl group:



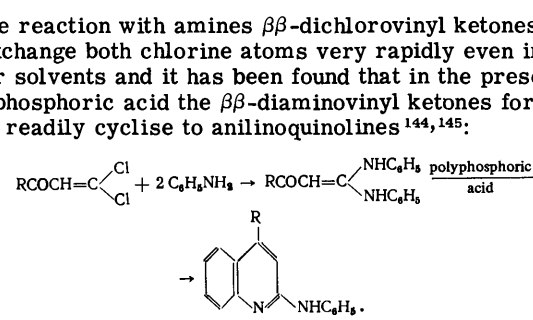
Under conditions analogous to those of reactions with ammonia, primary amines are ketovinylated with β-chlorovinyl ketones[64,120,131-137] and hydroxymethylene ketones[123,138]; ethynyl ketones can also be used[5,125]. In the presence of an excess of aromatic amines, the Schiff bases of β-arylaminovinyl ketones are formed as a rule[122,134,139-142]; they have been used for the synthesis of quinolines[139,140]:



Cyclic β-chlorovinyl ketones with a fixed *S-trans*-conformation react very readily with primary amines[122,143]:



In the reaction with amines ββ-dichlorovinyl ketones rapidly exchange both chlorine atoms very rapidly even in nonpolar solvents and it has been found that in the presence of polyphosphoric acid the ββ-diaminovinyl ketones formed very readily cyclise to anilinoquinolines[144,145]:



Similar results were obtained also with di- and tri-chloroacrolein[146]. In a number of cases the transamination of β-aminovinyl ketones was achieved[147,148]:

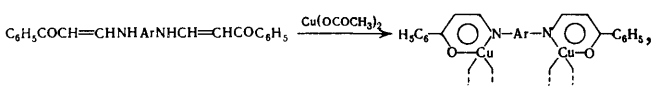
$$C_6H_5COCH=CHNHC_6H_5 + C_{10}H_7NH_2 \rightarrow C_6H_5COCH=CHNHC_{10}H_7 + C_6H_5NH_2.$$

The products of the ketovinylation of aromatic amines with aryl β-chlorovinyl ketones are difficult to purify by recrystallisation from the initial ketones. Therefore in

the synthesis of β-aminovinyl ketones of this kind water-soluble quaternary β-aroylvinyltrimethylammonium salts may be used as the ketovinylating agents [149,150]:

$$ArCOCH{=}CH\overset{+}{N}(CH_3)_3 + NH_2C_6H_5 \rightarrow ArCOCH{=}CHNHC_6H_5.$$

Carbonylvinylammonium salts have played a particularly important role in the synthesis of *NN'*-bisketovinylated aromatic diamines [149]. A synthesis of chelate polymers has been developed on the basis of such diamines:

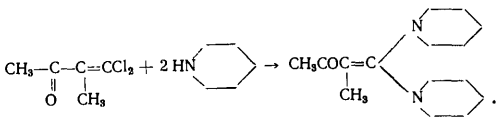


where Ar = $-C_6H_4-$ or $-(C_6H_4)_2-$. Using ammonium salts of the type $RCOCH{=}CH\overset{+}{N}(CH_3)_3Cl^-$, it proved possible to develop a method for the synthesis of hitherto unknown *N*-(β-acylvinyl)-substituted glycines and their ethyl esters [151]. The interaction of quaternary salts with the sodium salt and ester of glycine takes place very vigorously in aqueous solution.

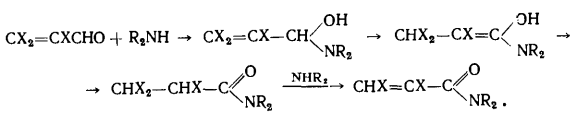
It is noteworthy that tautomerism of an interesting type, ketimine–enol ⇌ enamine–ketone, has been investigated in β-aminovinyl ketones obtained by the ketovinylation of ammonia and primary amines. Tautomerism of this type was investigated in detail by Nesmeyanov and coworkers [117,118,152,153], Potapov et al. [135], and Kazitsyna et al. [154]

Among secondary amines, aliphatic amines and saturated heterocycles are very readily ketovinylated. When they react with β-chlorovinyl ketones [64,120,155–157], ethynyl ketones [125,158], and hydroxymethylene ketones [123,159–162], β-dialkylaminovinyl ketones are formed.

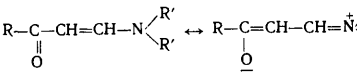
In the reaction with secondary amines both chlorine atoms of ββ-dichlorovinyl ketones [144,163] and dichloroacrolein [164] are substituted, but their α-alkyl derivatives react very slowly due to the breakdown of the coplanarity of the carbonyl group and the double bond [144,163]:



It is interesting to note that with polychlorinated acroleins the secondary amine attacks the carbonyl group. The subsequent allyl rearrangement and elimination of HX leads to the acid amide [165]:



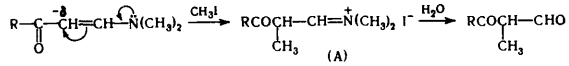
β-Dialkylaminovinyl ketones have high dipole moments [166]. For example, the dipole moment of methyl β-dimethylaminovinyl ketone is 5.67 D.



The capacity of these compounds to react with nucleophilic reagents is very weak (they react only with powerful nucleophilic reagents¶) and conversely their reaction with electrophilic reagents takes place readily. The electrophilic agent attacks the α-carbon atom of the double bond.

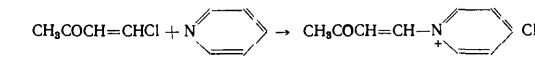
¶ For further details see pp. 434 and 447.

Thus, instead of the expected quaternary β-acylvinyltrimethylammonium salts, the methylation of β-dimethylaminovinyl ketones led to the isolation after hydrolysis of the decomposition products of salts of type (A) [156,167]. The synthesis of α-substituted β-keto-aldehydes is based on this reaction:

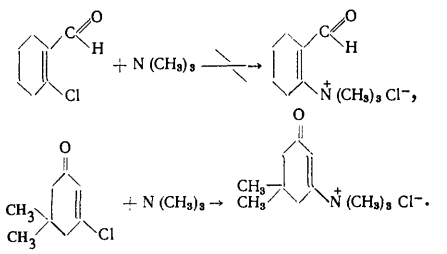


In an acid medium β-dialkylaminoacroleins [160] and β-dimethylaminovinyl ketones [168] exchange the α-hydrogen atom at the double bond for deuterium. Their capacity to enter into the ketovinylation reaction has already been mentioned (see p. 434).

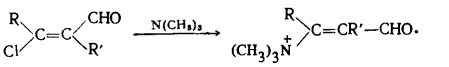
The ketovinylation reaction of tertiary amines occupies a special place, primarily because extremely powerful ketovinylating agents—β-acylvinylammonium salts—were obtained on its basis. A quaternary salt of this type was obtained for the first time by Yakubovich and Merkulova [169] by the action of pyridine on β-chlorovinyl methyl ketone:



Subsequently Kochetkov, Skoldinov, and coworkers [170,171] found a general method for the ketovinylation of tertiary amines with β-chlorovinyl ketones†. Nesmeyanov and Rybinskaya [66] suggested that the same trimethyl- and triethyl- ammonium salts be used without preliminary purification for the ketovinylation of the cyanide ion. It is interesting to note that cyclic β-chlorovinyl carbonyl compounds known to have the *cis*-configuration hardly react with tertiary amines [172,173], while ketones with a fixed *trans*-configuration are converted into quaternary salts with almost quantitative yields [172]:



αβ-Dialkyl-β-chlorovinylaldehydes react with trimethylamine very slowly and the quaternary ammonium salts are then obtained with very low yields [173–175]:



The possibility, in principle, of synthesising quaternary salts by the reaction of ethynyl ketones with tertiary amine hydrochlorides has been demonstrated for ethynyl phenyl ketone as the sole example [127]:

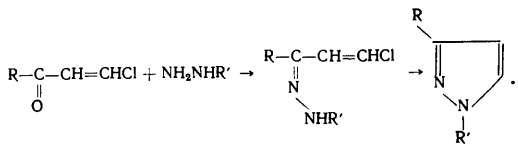
$$C_6H_5COC{\equiv}CH + N(CH_3)_3 \cdot HCl \rightarrow C_6H_5COCH{=}CH\overset{+}{N}(CH_3)_3\,Cl^-.$$

Hydrazines, semicarbazide, and hydroxylamine are much more powerful bases and nucleophilic agents than amines because of the additional electron transfer to the

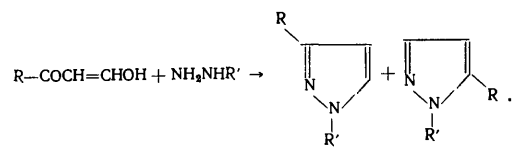
† Because of a number of disadvantages of experiments with β-chlorovinyl ketones, largely due to the high toxicity of these compounds, the above workers suggested that the ketones be converted into quaternary ammonium salts without being isolated from the reaction mixture [171].

nitrogen atom by the adjacent NH_2 and OH groups. It has been found that, in contrast to amines, these reagents are capable of attacking a second electrophilic centre in the β-chlorovinyl ketone molecule, i.e. the carbonyl group (cf. the reactions with RLi and RMgX, p. 434). The capacity to attack the carbonyl group is more pronounced in hydrazines and semicarbazides than in hydroxylamine. The latter is a weaker base and nucleophilic agent and reacts simultaneously with both electrophilic centres. It is noteworthy that the ketovinylation of these compounds leads in most cases to heterocyclic pyrazole and isoxazole systems, the position of the substituents in which shows the direction of the primary attack by the nucleophilic agent.

Nesmeyanov et al.[2] have shown that alkyl β-chlorovinyl ketones react with hydrazine and alkyl hydrazines with formation of 3-alkyl- and 3-alkyl-1-aryl-pyrazoles:

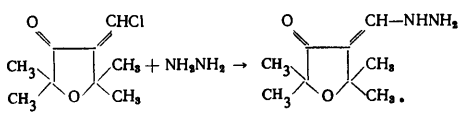


This result is evidence in the first place that the reaction begins with attack on the carbonyl group. This was subsequently confirmed by the isolation of the intermediate hydrazones[16,176,177], which subsequently cyclised to the pyrazole ring. Furthermore, the use of the β-chlorovinyl ketones in this reaction is of practical value, since it provides a preparative method for the synthesis of 1,3-disubstituted pyrazoles. The hydroxymethylene ketones employed previously yield a mixture of 1,3- and 1,5-disubstituted pyrazoles.[178]



Subsequently the reaction was extended also to other aromatic, aliphatic,[90,176] and barene[179] β-chlorovinyl ketones and αβ-disubstituted β-chlorovinyl aldehydes[180,181]. The unsubstituted pyrazole was obtained with the aid of β-halogenoacroleins[182-184]. The reactions with polyhalogenoacroleins and poly(chlorovinyl ketones) also yield hydrazones, which are converted into the corresponding pyrazoles on boiling[185-187], the yield of pyrazole increasing with the degree of chlorination of the ketovinylating agent[187]. In this connection it is interesting to note that cyclic *cis*-β-chlorovinyl ketones (for example, 1-acyl-2-chlorocyclopent-1-ene) readily form hydrazones, which, however, do not cyclise to pyrazoles[188]. This is because of the lower lability of the halogen in the *cis*-configuration.

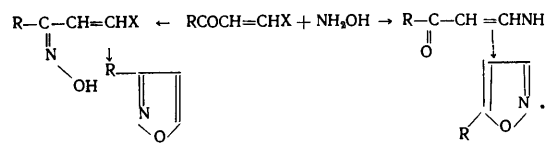
The only known case of *N*-ketovinylation of hydrazine is the reaction with a β-chlorovinyl ketone, the approach to the carbonyl group of which is sterically hindered[189]:



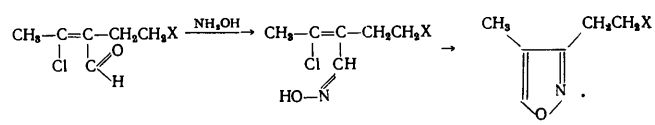
In this connection we may recall that a powerful nucleophilic agent such as RMgX also does not usually react with the carbonyl group of β-chlorovinyl ketones if the approach to the latter is hindered, and attacks the β-carbon atom of the double bond[22-25]. Finally, it should be noted that ethynyl ketones have also been used for the synthesis of pyrazoles[190].

Semicarbazide also reacts with β-chlorovinyl ketones at the carbonyl group with formation of semicarbazones[16,169,191-193]. Like hydrazones, semicarbazones can probably cyclise to the corresponding 1-carbamoylpyrazoles, since it was found that they undergo a change on recrystallisation[169].

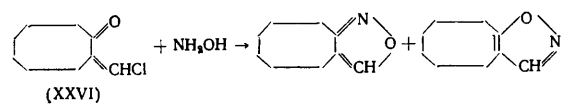
Hydroxylamine is less basic and less nucleophilic and therefore in the reaction with β-chlorovinyl[179,194-196], β-phenoxyvinyl[196], β-phenylthiovinyl[196], and β-hydroxyvinyl[197] ketones it attacks both electrophilic centres simultaneously. Subsequent cyclisation leads to the formation of a mixture of 3- and 5-substituted isoxazoles. Similar results were obtained also with barenylmethyl β-chlorovinyl ketones[179]:



β-Halogenoacroleins have been suggested for the synthesis of unsubstituted isoxazoles[182-184,194]. It is interesting to note that in the reaction of β-alkyl substituted β-chloroacroleins under mild conditions it is possible to isolate oximes[172], while on heating isoxazoles are formed immediately[180,181]:

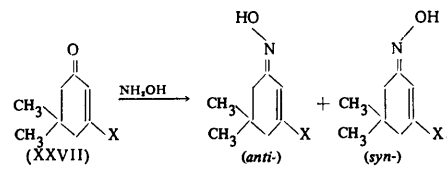


The cyclic β-chlorovinyl ketone (XXVI), with a fixed cisoid conformation, reacts with hydroxylamine to form a mixture of isoxazoles similar to that obtained in the reaction with the corresponding hydroxymethylene ketone[198,199].



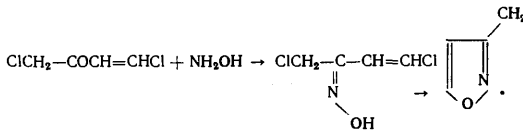
(XXVI)

However, in the reaction of hydroxylamine with the β-chlorovinyl ketone (XXVII), which has a fixed transoid conformation, only oximes (*syn*- and *anti*-isomers) are formed. In this case attack on the electrophilic centre of the double bond is hindered, since the double bond is located in the ring. Furthermore, the fixed transoid conformation prevents cyclisation[172]:

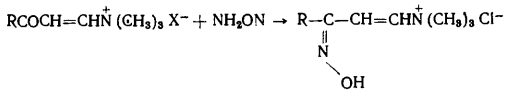


By varying the ketovinylating agents, it is possible to alter the mode of reaction with hydroxylamine. An increase in the electrophilicity of the carbonyl group in alkyl β-chlorovinyl ketones by the introduction of electron-acceptor substituents in the α-position of the alkyl group

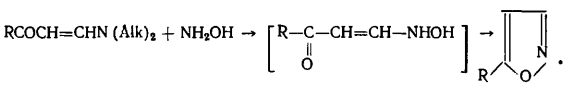
leads to the preferential formation of 3-substituted isoxazoles [195,200]‡. This shows that an oxime is formed as an intermediate in the main reaction:



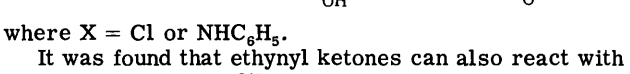
A similar effect can probably be achieved by replacing the chlorine atom in β-chlorovinyl ketones by a quaternary ammonium group. In this case the corresponding oximes could be obtained under very mild conditions [172]:



On the other hand, by introducing into the α-position a powerful electron-donor group $N(Alk)_2$ (instead of chlorine), which suppresses the electrophilic activity of the carbonyl group, the entire process may be reduced to the formation of 5-substituted isoxazoles only, i.e. products of the *N*-ketovinylation of hydroxylamine will form in the first stage of the reaction [52,196]:

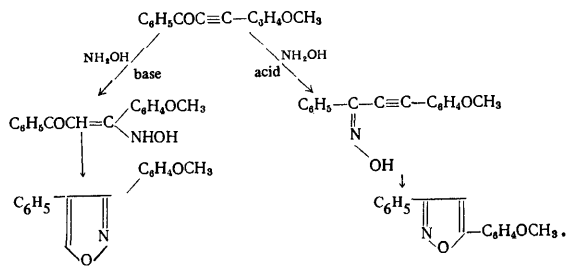


When *N*-phenyl-substituted hydroxylamine is used, only *N*-ketovinylation products are formed [147]:

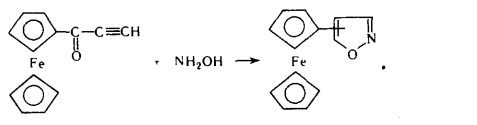


where X = Cl or NHC_6H_5.

It was found that ethynyl ketones can also react with formation of isoxazoles [202]. As in the case of β-chlorovinyl ketones, this reaction takes place in two ways, but, by varying the conditions, the process can be driven one way or another. In an acid medium attack on the carbonyl group is facilitated and in an alkaline medium the 1,4-addition (*N*-ketovinylation) product is formed as an intermediate:



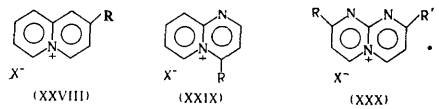
Ferrocenyl-substituted isoxazole was obtained in the same way [190]:



‡ We may recall that Kochetkov and Khomutova [201] developed a method of synthesis based on the reaction of hydroxylamine with β-keto-acetals (ω-acylmethyldioxolanes). An oxime is formed as an intermediate in the reaction, which permits the selective synthesis of trisubstituted isoxazoles.

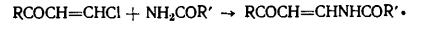
We may also recall the synthesis of certain nitrogenous six-membered heterocycles using guanidine, alkylamidines, urea, thiourea, α-aminopyridine, 2-aminopyridine, etc. Thus, on heating, β-chlorovinyl ketones [203,204] and β-halogenoacroleins [182,184,205] react with guanidines in a strongly acid medium with formation of 2-aminopyrimidine derivatives. However, in this case the site of the primary attack by the nucleophilic agent cannot be deduced, since the intermediate products were not isolated. The use of thiourea in this reaction leads to the formation of 2-mercaptopyrimidine [184].

A method of synthesis of heterocyclic cations containing an ammonium nitrogen atom in the bridge—dehydroquinolizinium salts and their 1-aza- and 1,9-diaza-analogues [compounds (XXVIII), (XXIX), and (XXX) respectively]—has been developed on the basis of β-chlorovinyl ketones and their derivatives—β-keto-acetals [206-209]:

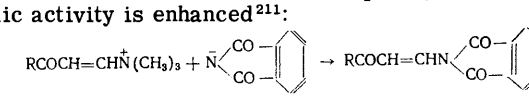


(XXVIII) (XXIX) (XXX)

The ketovinylation of carboxylic acid amides is difficult and requires heating to 180–200°C, the yields of products being low (8–22%): [210]

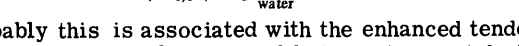


However, the anions of acid amides, for example, the phthalimide ion, are successfully ketovinylated when quaternary β-acylvinyltrimethylammonium salts are used. This reaction takes place at room temperature, and with β-aroylvinyltrimethylammonium salts aqueous solutions may be employed. On the other hand, with quaternary aliphatic ammonium salts [$AlkCOCH{=}CH\overset{+}{N}(CH_3)_3X^-$] the phthalimide ion is much too weak a nucleophilic agent in water and therefore the reaction must be carried out in a dipolar aprotic solvent—dimethylformamide (DMFA). [151] The anions are known to be much less solvated in solvents of this kind than in water and consequently their nucleophilic activity is enhanced [211]:



where R = Ar (solvent—water) or R = alkyl (solvent—dimethylformamide). The structure of the compounds obtained was demonstrated by hydrolysis to the corresponding β-aminovinyl ketones [151].

Carbonylvinylammonium salts proved to be completely irreplaceable in the synthesis of β-nitrovinyl ketones [66]. It is noteworthy that, despite all attempts, β-chlorovinyl ketones could not be made to react with the nitrite ion. The reaction of the quaternary salts with the nitrite ion was carried out in aqueous solution, potassium dihydrogen phosphate being added as a buffer. The buffer solution is necessary because the aryl β-nitrovinyl ketones formed are very sensitive to the action of hydroxide ions, the concentration of which increases as trimethylamine is eliminated. It was found that the yield of aryl β-nitrovinyl ketones falls as the electron-acceptor properties of the substituent in the phenyl ring become more pronounced:



Probably this is associated with the enhanced tendency of the resulting aryl β-nitrovinyl ketones to react further with the nucleophilic agents present in the reaction mixture. Thus the yield of β-nitrovinyl *p*-tolyl ketone is 45%, [212] while *p*-nitrophenyl β-nitrovinyl ketone was obtained in a yield of only 3%. [150]

The *N*-ketovinylation of the axide ion occupies a special position, since it led to possibilities of interest not only for syntheses but also for theory. Since these data were obtained in connection with the study of the stereochemistry of ketovinylation and the effect of groups eliminated on substitution, they will be discussed in detail in a later section (see section IV).

3. *S*-Ketovinylation

Methods for the *S*-ketovinylation have been developed comparatively little. Among these the ketovinylation of RS ions (R = alkyl or aryl), which are very powerful nucleophilic agents, has been investigated in greatest detail. It has been found that the reaction of thiophenoxides with β-halogenovinyl ketones yields β-phenylthiovinyl ketones[213]. Montanari and coworkers[214,215], who investigated the stereochemistry of this reaction, noted that the geometrical configuration of the initial ketone is retained on substitution. The reaction of course takes place more readily than with phenols. In some cases it was found that the halogen is very readily exchanged for an alkanethiolate ion even in benzene solution[216]:

$$RCOCH{=}CHCl + R'S^- \xrightarrow{H^+} RCOCH{=}CHSR' \xrightarrow{R'SH} RCOCH_2CH(SR')_2.$$

When an excess of mercaptans is used in the reaction, the latter does not stop at the β-alkylthiovinyl ketone stage, since a second mercaptan molecule adds to the double bond. This results in the formation of β-keto-mercaptals[217] (cf. the *O*-ketovinylation of OR^- in the presence of ROH):

$$RCOCH{=}CHCl + \bar{S}Alk \rightarrow RCO\bar{C}H{-}CH\!\!\begin{matrix}Cl\\ SAlk\end{matrix} \rightarrow$$

$$\rightarrow RCOCH{=}CHSAlk \xrightarrow{\bar{S}Alk} RCO\bar{C}H{-}CH\!\!\begin{matrix}SAlk\\ SAlk\end{matrix} \xrightarrow{H^+} RCOCH_2CH(SAlk)_2.$$

It was found that under these conditions the reaction with ethane-1,2-dithiol yields cyclic β-keto-mercaptals[217]. The corresponding β-ethylthiovinyl and β-phenylthiovinyl ketones were obtained also with ethynyl ketones as the ketovinylating agents in the presence of basic catalysts[125].

A brief communication has been published on the synthesis of mercaptals when mercaptans react with β-hydroxyvinyl ketones in an acid medium[218].

Phenylthio-derivatives are oxidised with hydrogen peroxide to the corresponding sulphoxides and sulphones[219]:

$$RCOCH{=}CHSC_6H_5 \xrightarrow{H_2O_2} RCOCH{=}CHSOC_6H_5 \xrightarrow{H_2O_2} RCOCH{=}CHSO_2C_6H_5.$$

The latter can also be obtained directly by the ketovinylation of the benzene sulphinate ion[219]:

$$C_6H_5COCH{=}CHCl + \bar{S}O_2C_6H_5 \rightarrow C_6H_5COCH{=}CHSO_2C_6H_5.$$

ββ-Dichlorovinyl methyl ketone reacts with sodium benzenesulphinate in a very unusual manner. Diphenylsulphonylmethane was obtained as the main product[65] together with a small amount of 1-chloro-1-phenylsulphonylbuten-3-one:

$$CH_3COCH{=}CCl_2 + C_6H_5\bar{S}O_2 \rightarrow CH_3COCH{=}C\!\!\begin{matrix}SO_2C_6H_5\\ Cl\end{matrix} + CH_2\!\!\begin{matrix}SO_2C_6H_5\\ SO_2C_6H_5\end{matrix}.$$

The formation of diphenylsulphonylmethane can be explained by the rapid hydrolysis of the intermediate 1,1-diphenylsulphonylbuten-3-one:

$$CH_3COCH{=}C\!\!\begin{matrix}SO_2C_6H_5\\ SO_2C_6H_5\end{matrix} + \bar{O}H \rightarrow CH_3COCH(\bar{O})C\!\!\begin{matrix}SO_2C_6H_5\\ SO_2C_6H_5\end{matrix} \rightleftarrows$$

$$\rightleftarrows CH_3{-}COCH(\underline{O}){-}CH\!\!\begin{matrix}SO_2C_6H_5\\ SO_2C_6H_5\end{matrix} \rightarrow \bar{C}H\!\!\begin{matrix}SO_2C_6H_5\\ SO_2C_6H_5\end{matrix} + (?)\ CH_3COCOH$$

$$\downarrow H^+$$

$$CH_2(SO_2C_6H_5)_2.$$

Another method of ketovinylation, using ethynyl ketones, may be successfully employed for the synthesis of β-keto-sulphones[125,200]. However, the most convenient ketovinylating agents for this purpose proved to be the quaternary ammonium salts $RCOCH{=}CH\overset{+}{N}(CH_3)_3Cl^-$. The reaction, carried out in an aqueous medium, results in a very rapid (literally on mixing the solutions!) formation of the sulphone with a high yield[221]. Ketovinylation with the aid of quaternary carbonylvinylammonium salts has the advantage that the product is obtained immediately in a pure form and does not contain the starting material as an impurity, as happens when aryl β-chlorovinyl ketones are employed. Since both the initial quaternary salts and the resulting sulphones have the *trans*-configuration, it was concluded that the configuration is retained on substitution of the $\overset{+}{N}(CH_3)_3$ group. However, the reaction was not investigated with *cis*-derivatives, since quaternary *cis*-β-acylvinyltrimethylammonium salts are so far unknown.

The ketovinylation of the sulphide ion has been demonstrated with the β-butyrylvinylammonium salt as an example[66]. The doubly charged sulphide ion is then ketovinylated twice and bis-(β-butyrylvinyl) sulphide was isolated in 88% yield:

$$2C_3H_7COCH{=}CH\overset{+}{N}(CH_3)_3 + S^{2-} \rightarrow (C_3H_7COCH{=}CH)_2S.$$

Despite the attempts made, this reaction could not be stopped at the mono-ketovinylation stage. This could not be done even when sodium hydrogen sulphide was employed[222]. Mono-ketovinylation could be achieved only by the reaction of β-chlorovinyl ketones with thioacetate salts. β-Acylethylenethiol is obtained after the hydrolysis of the reaction product[222]:

$$C_4H_9COCH{=}CHCl + CH_3COSNa \rightarrow C_4H_9COCH{=}CHSCOCH_3 \xrightarrow{NaSH} C_4H_9COCH{=}CHSH.$$

It is interesting to note that, according to the data of Nesmeyanov et al.[65], the analogous reaction with ββ-dichlorovinyl ketone yields a thioketen dimer after hydrolysis and elimination of hydrogen chloride:

$$CH_3COCH{=}CCl_2 + CH_3COSNa \rightarrow \left[CH_3COCH{=}C\!\!\begin{matrix}Cl\\ SCOCH_3\end{matrix} \xrightarrow{H_2O} CH_3COCH{=}C\!\!\begin{matrix}Cl\\ SH\end{matrix}\right] \xrightarrow{-HCl}$$

$$\rightarrow [CH_3COCH{=}C{=}S]_2.$$

In the synthesis of β-acylethylenesulphonates it was found that quaternary carbonylvinylammonium salts are the only possible ketovinylating agents, since in their reaction with the SO_3^{2-} ion in an aqueous medium they are sparingly soluble mixed salts of type (XXXI), which makes it possible to stop the reaction at the first stage. The mixed salts (XXXI) can be converted into alkali metal salts be subsequent treatment with KBF_4, KCN, or $NaNO_3$:[221]

$$RCOCH{=}CH\overset{+}{N}(CH_3)_3 + SO_3^{2-} \rightarrow RCOCH{=}CHSO_3^-\overset{+}{N}(CH_3)_3CH{=}CHCOR \xrightarrow{KBF_4}$$

$$\rightarrow RCOCH{=}CHSO_3K\ (soln.) + RCOCH{=}CH\overset{+}{N}(CH_3)_3\bar{B}F_4\ (ppt.).$$

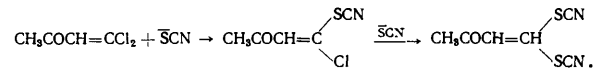
On the other hand, in the synthesis of hitherto unknown salts of phenylacylmethionic acids the fact that with β-chlorovinyl ketones the reaction proceeds further was employed[221,223]:

$$RCOCH{=}CHCl + Na_2SO_3 + NaHSO_3 \rightarrow RCOCH_2CH(SO_3Na)_2.$$

The interaction of β-chlorovinyl ketones with thiocyanate ions may be included among the *S*-ketovinylation reactions. This reaction was achieved for the first time by Panizzi[64] in only one case. It was developed further by Kochetkov[224], who employed a number of alkyl β-chlorovinyl ketones, and by the author of a patent[225], who described the use of ring-substituted aryl β-chlorovinyl ketones:

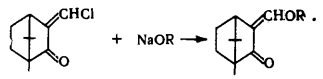
$$RCOCH{=}CHCl + \bar{S}CN \rightarrow RCOCH{=}CHSCN.$$

Nesmeyanov et al.[65] showed that ββ-dichlorovinyl ketones react with the thiocyanate ion, both chlorine atoms being substituted. Also it was possible to isolate the intermediate monosubstituted product:



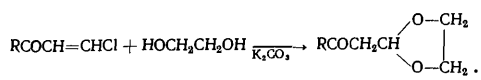
4. *O*-Ketovinylation

The first information about the ketovinylation of OR^- ions appeared in the patent literature in 1937[226-228]. The interaction of β-chlorovinyl ketones with alcohols in the presence of alkaline reagents was investigated in greater detail by Nesmeyanov et al.[229] and simultaneously by Price and Pappalardo[177]. These workers showed that the reaction with alkoxide ions in the corresponding alcohols does not as a rule stop at the substitution stage, the alcohol adding subsequently to the double bond of the intermediate β-alkoxyvinyl ketones. This results in the formation of β-keto-acetals in yields of 50–90%. Furthermore, it was found that β-keto-acetals are formed in low yields also when hydrogen chloride is employed as the catalyst[229]. The intermediate β-alkoxyvinyl ketone was isolated only in the case of the less reactive chloromethylenecamphor[230]:

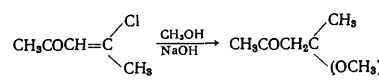


Therefore β-alkoxyvinyl ketones must be obtained by the elimination of the alcohol from the β-keto-acetals using various basic and acid catalysts[231-235].

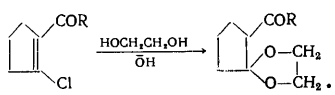
In recent years the synthesis of β-keto-acetals has been extended to higher aliphatic[230,236-239] and heterocyclic[239] homologues. The use of glycols in these reactions lead to the development of a method for the synthesis of stable dioxolane derivatives[233,240]:



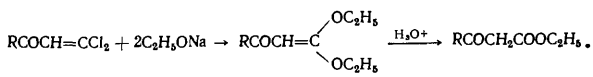
It is noteworthy that β-alkyl-substituted β-chlorovinyl ketones also react with alkoxides, albeit with difficulty, forming monoketals of β-diketones[139]:



Even the relatively unreactive cyclic β-chlorovinyl ketones with a fixed *cis*-configuration react with ethylene glycol in the presence of alkaline agents forming monoketals[188]:



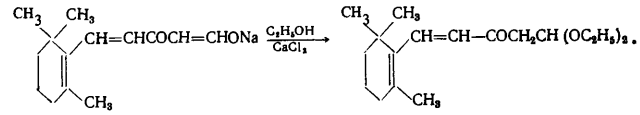
In ββ-dichlorovinyl ketones both chlorine atoms are exchanged for alkoxy-groups. In an anhydrous medium this results in the formation of β-dialkoxyvinyl ketones[65,139,163], which are readily hydrolysed to acylacetate esters[65]:



When alcoholic solutions of alkalis were allowed to react with ethynyl ketones, β-keto-acetals were also obtained[128].

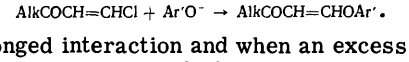
Hydroxymethylene ketones too can be used for the synthesis of β-keto-acetals, but in this case it is necessary to employ acid catalysts[241-247]. Royals and Brannok[248] made a detailed study of the reaction of the sodium salts of hydroxymethylene ketones with alcohols in the presence of hydrochloric acid and found that, depending on the structure of the initial ketones, acetals or β-alkoxyvinyl ketones are formed.

β-Keto-acetals with a fairly complex structure were obtained similarly[249]:



β-Keto-acetals have been used as intermediates for the synthesis of a wide variety of compounds. In particular, they have been employed for the preparation of certain heterocycles[9,250,251]: they are used very often for the synthesis of various derivatives formed by the reaction of the carbonyl group[252,253]. Higher members of the $RCOCH_2CH(OR')_2$ series, where $R = C_9-C_{12}$, have the scent of oranges and therefore it is suggested that they be employed in cosmetics and in the manufacture of perfumed soap[254].

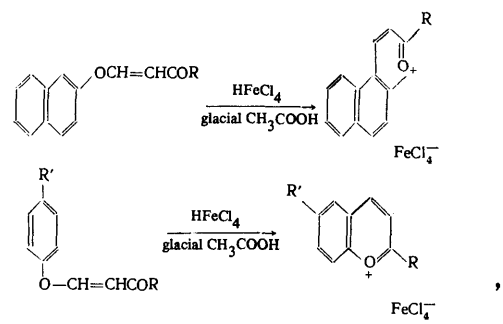
In contrast to alcohols, the reaction of β-chlorovinyl ketones with phenols may be stopped at the first stage, which leads to the formation of β-aryloxyvinyl ketones[62]. It has been shown for alkyl β-chlorovinyl ketones that this reaction is general and is catalysed by alkaline agents in various solvents (water, dioxan, excess of phenol):



During prolonged interaction and when an excess of phenol is used, the reaction proceeds further to some extent, yielding the acetals of β-keto-aldehydes[229] as in the case of alcohols.

The reaction of β-chlorovinyl ketones with sodium β-naphthoxide differs significantly from that described above. Both in aqueous alkali and in dioxan the products of *C*-ketovinylation at the α-carbon atom of the naphthalene ring were isolated[61] together with the *O*-ketovinylation products (see p. 436).

Nesmeyanov et al.[91] showed that the most interesting property of β-aryloxyvinyl ketones is their capacity to undergo a rearrangement analogous to the Fries rearrangement. It was found that, on treating solutions of β-phenoxyvinyl ketones in glacial acetic acid with a solution of iron(III) chloride in concentrated hydrochloric acid, the chloroferrates(III) of 2-substituted benzo- and naphthopyrylium cations are formed. The isomeric 4-substituted pyrylium salts are not produced. Thus it was shown that the products of the *O*-ketovinylation of phenols rearrange in an acid medium to *C*-ketovinylation products:

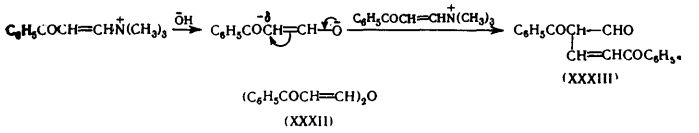


the rearrangement occurring not only in the *ortho*-position but also in the *para*-positions of the phenol ring, if the

latter is free. We may recall that the same pyrylium salts were obtained also by the direct condensation of β-chlorovinyl ketones with phenols and naphthol[88,89].

Finally, it should be noted that nucleophilic addition to ethynyl ketones has also been employed for the *O*-ketovinylation of phenols. Thus Bowden et al.[125] observed the nucleophilic addition of phenols to ethynyl ketones in the presence of bases.

The ketovinylation of the OH^- ion by any of the ketovinylating agents takes place in a complex manner and as a rule results in the formation of ketones (hydrolytic decomposition)[26]. β-Aroylvinyltrimethylammonium salts are an exception. They readily react with aqueous solutions of weak bases and even with water, which sometimes results in complications if the ketovinylation is carried out in an aqueous medium. This leads to products in which there are two carbonylvinyl residues per oxygen atom derived from water. This was noted for the first time by Kochetkov et al.[170] They found that β-benzoylvinyltrimethylammonium chloride undergoes "hydrolysis" in aqueous solution under the action of sodium bicarbonate with formation of a compound for which two alternative structures were proposed on the basis of elemental analysis and molecular weight measurements: either the structure of the β-benzoylvinyl ether (XXXII) or benzoyl(β-benzoylvinyl)acetaldehyde (XXXIII). According to infrared spectroscopic data, the latter is the most likely structure[151], but is complicated by the occurrence of ring–chain tautomerism. It is suggested that the decomposition of the quaternary salt with water is accompanied by successive *O*- and *C*-ketovinylation according to the mechanism

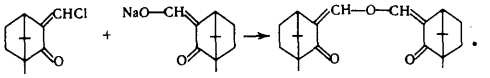


(XXXIII)

$(C_6H_5COCH{=}CH)_2O$

(XXXII)

It is interesting to note that, in contrast to β-aroylacetaldehyde, the enolates of hydroxymethylenecamphor are ketovinylated at the oxygen atom[63]:



The "hydrolysis" is particularly facilitated by the presence of electron-acceptor groups in the aryl ring. Thus β-aroylvinyltrimethylammonium chlorides containing halogen atoms in the *ortho*- or *para*-positions are "hydrolysed" even as a result of atmospheric moisture during storage and consequently these compounds cannot be stored in aqueous solutions. The mechanism of the "hydrolysis" changes sharply when one methyl group in the quaternary salts is replaced by the benzyl group[151]:

$$C_6H_5COCH{=}\overset{+}{N}H(CH_3)_2CH_2C_6H_5 \xrightarrow{H_2O} C_6H_5COCH{=}NH(CH_3)_2 + C_6H_5CH_2OH.$$

The weakly nucleophilic acetate ion could not be made to undergo the ketovinylation reaction for a long time. This became possible only when powerful ketovinylating agents such as β-acylvinyltrimethylammonium salts were employed. In order to avoid "hydrolytic" side processes, it is necessary to employ dry dipolar solvents such as dimethylformamide. In glacial acetic acid the process does not stop at the ketovinylation stage and acylals of β-ketoaldehydes are formed[151]:

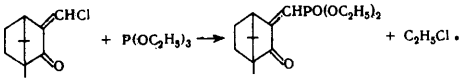
$$RCOCH{=}\overset{+}{N}H(CH_3)_2 + \overline{O}COCH_3 \rightarrow RCOCH{=}CHOCOCH_3 \xrightarrow{CH_3COOH} \rightarrow RCOCH_2CH(OCOCH_3)_2.$$

5. *P*-Ketovinylation

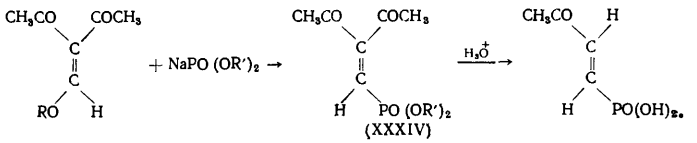
Ketovinylation of a phosphorus–carbonylvinyl group bond has been investigated extremely little and its possibility in principle has been demonstrated in only a few instances. In 1959 Kreutzkamp and Schindler[255] found that β-chlorovinyl methyl ketone undergoes the Michaelis–Arbuzov reaction with tributyl phosphite, forming dibutyl β-acetylvinylphosphonate:

$$CH_3COCH{=}CHCl + P(OC_4H_9)_3 \rightarrow CH_3COCH{=}CH{-}PO(OC_4H_9)_2 + C_4H_9Cl.$$

They showed further that chloromethylenecamphor[256] reacts likewise:



A similar phosphonic acid derivative (XXXIV) was obtained also with β-alkoxyvinyl diketone, subsequent treatment with the acid (XXXIV) leading to the formation of β-acetylvinylphosphonic acid[255,257]:



(XXXIV)

Nifant'ev et al.[258] suggested the reaction with triphenylphosphine for the identification of β-chlorovinyl methyl ketone. The structure of a phosphonium salt was attributed to the product of this reaction.

6. Ketovinylation at a Halogen Atom

The synthesis of β-chlorovinyl ketones from hydroxymethylene ketones under the action of thionyl chloride may be regarded formally as ketovinylation at a halogen atom. The chlorine atoms in β-chlorovinyl ketones are replaced by other halogens on reaction with iodide and fluoride ions. Since these ions are insufficiently nucleophilic in proton-containing media (particularly the fluoride ion!), the exchange of chlorine is carried out in aprotic dipolar solvents. Kochetkov showed[224] that the exchange with sodium iodide takes place fairly smoothly in acetone with formation of alkyl β-iodovinyl ketones. Subsequently it was shown by infrared and proton spin resonance spectroscopy that in this case the initial *trans*-configuration is retained[173]: *trans*-AlkCOCH=CHCl+I^- → AlkCOCH=CHI-*trans*. The exchange of chlorine for fluorine atoms has been recently achieved in α-methyl-substituted β-chlorovinyl phenyl ketone. Dimethylformamide was used as the solvent:

$$C_6H_5COC(CH_3){=}CHCl + F^- \xrightarrow{DMFA} C_6H_5CO(CH_3)C{=}CHF.$$

β-Bromovinyl ketones were not obtained by the exchange reaction, but their synthesis was achieved by another ketovinylation procedure—using ethynyl ketones[125,158,214]. Bowden et al.[125,158] obtained these compounds by the addition of hydrogen bromide to the triple bond of ethynyl ketones. β-Chlorovinyl ketones can be obtained similarly[215].

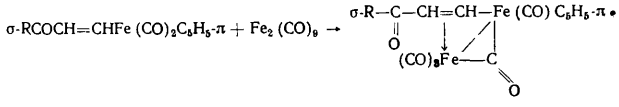
7. *Fe*-Ketovinylation

The ketovinylation of anions containing metals is of considerable interest. Complex anions of transition metals may be sufficiently nucleophilic among these.

In order to synthesise organoiron compounds containing the carbonylvinyl group linked by a σ bond to the iron atom, a study was made of the ketovinylation of the anion $[Fe(CO)_2C_5H_5\text{-}\pi]^-$.[259] Since according to Dessy's data[260] the nucleophilicity of this anion is close to that of the thiophenate ion, β-chlorovinyl ketones, which are known to react smoothly with thiophenate ions[213,214] were chosen as the ketovinylating agents:

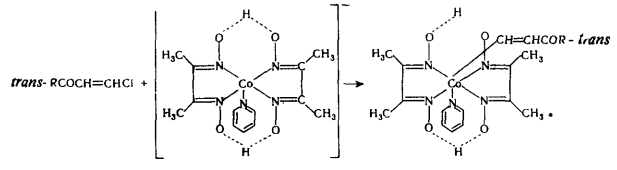
$$RCOCH{=}CHCl + Na^+[Fe(CO)_2C_5H_5]^- \rightarrow \sigma\text{-}RCOCH{=}CH{-}Fe(CO)_2C_5H_5\text{-}\pi .$$

The resulting complexes σ-RCOCH=CHFe=$(CO)_2C_5H_5$-π proved to be interesting objects for the investigation of the synthesis of mixed σ–π complexes with Fe–Fe bonds. The latter are formed when σ-RCOCH=CHFe$(CO)_2C_5H_5$-π reacts with iron nonacarbonyl[261]:



8. *Co*-Ketovinylation

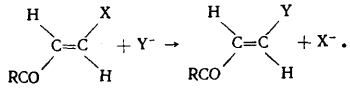
A complex anion of a fundamentally different type—pyridinatocobaloxime—was used to synthesise σ complexes with carbonylvinyl–cobalt bonds. Since the stability of this ion in water is evidence of its relatively low basicity, β-chlorovinyl ketones were chosen as ketovinylating agents[262]:



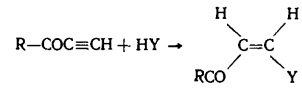
As for the ion $[Fe(CO)_2C_5H_5\text{-}\pi]^-$, it was found that the configuration is retained on substitution in the *trans*-series. It is interesting to note that the Co–CH=CHCOR bond in these complexes readily dissociates under the action of halogens. When the complexes are treated with iodine, *trans*-β-iodovinyl phenyl ketone and the corresponding complex with a Co–I bond are formed. Since the initial σ-(β-benzoylvinyl)pyridinatocobaloxime also had the *trans*-configuration, it was suggested that in this type of dissociation of the carbonylvinyl–cobalt bond the configuration is preserved.

III. CHOICE OF β-KETOVINYLATING AGENT

It follows from the studies reviewed that the correct choice of reagents is important for successful β-ketovinylation. The choice of the ketovinylating agent is determined mainly by the chemical and steric structure of the αβ-unsaturated ketone obtained, the nature of the attacking nucleophilic agent, and the possibility of a particular reaction mechanism. For example, in the synthesis of β-substituted vinyl ketones of the *trans*-series, the first β-ketovinylation method is used, i.e. the nucleophilic substitution reaction with the compounds *trans*-RCOCH=CHX, since it has been demonstrated in numerous instances[32,33,66,150,221,259] that the geometrical configuration is preserved on substitution:



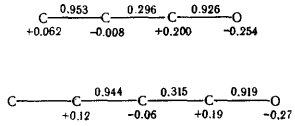
On the other hand in the synthesis of *cis*-isomers one uses as a rule nucleophilic addition to ethynyl ketones (second ketovinylation method), which leads to a *trans*-adduct[125,214,215]:



It is noteworthy that the first method is in principle suitable also for the synthesis of *cis*-isomers[211,215], but ketovinylating agents such as *cis*-β-chlorovinyl ketones are difficult to obtain and are usually synthesised by the addition of hydrogen halides to ethynyl ketones. Various β-substituted vinyl ketones, such as β-chloro- and β-amino-vinyl ketones and β-acylvinyltrialkylammonium salts, are most often used as ketovinylating agents, since nucleophilic addition to the triple bonds of ethynyl ketones does not allow the synthesis of, for example, compounds of the type RCOCR′=CHR″ or RCOCR′=CR″R‴. Furthermore, it is important to note that ethynyl ketones are themselves difficult to obtain.

In choosing the ketovinylating agent it is essential to take into account the selectivity of nucleophilic agents in relation to the particular electrophilic centre. In αβ-unsaturated carbonyl-containing compounds there are at least two electrophilic centres§: the carbonyl carbon atom and the β-carbon atom of the double bond, the electron density of the former being much lower than at the latter. Calculation of molecular diagrams of αβ-unsaturated ketones[265] by the LCAO MO method shows that the partial charge on the carbonyl carbon atom greatly exceeds the positive charge on the carbon atom of the double bond.

Molecular diagrams of the αβ-unsaturated oxo-compounds[265]

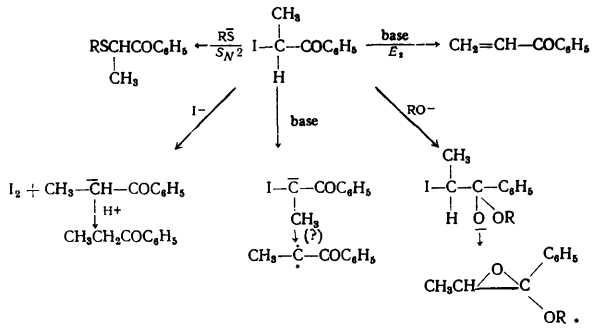


The numerals over the bonds indicate the bond orders and those over the atoms the charges. This calculation is evidently consistent with the empirical rule of vinylogy.

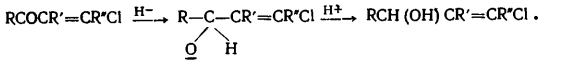
The study of nucleophilic reactivity has shown that nucleophilic agents are selective in relation to an electrophilic centre of a particular type and in the presence of several electrophilic centres in the same molecule various sites of nucleophilic attack are possible depending on the nature of the nucleophilic agent[266,267]. As an illustration,

§ It is also necessary to bear in mind a third possibility: the attack by the nucleophilic agent on the α-carbon atom. However, this probably occurs with much greater difficulty in the case of αβ-unsaturated ketones. For example, Kursanov and Parnes[263] showed that αβ-unsaturated ketones $ArCO\underset{\alpha}{C}H{=}\underset{\beta}{C}H{-}\underset{\gamma}{C}<$ without hydrogen atoms at the C_γ atom do not undergo hydrogen exchange under the action of bases. Miller and Lee[264] arrived at a similar conclusion concerning the derivatives of αβ-unsaturated carboxylic acids.

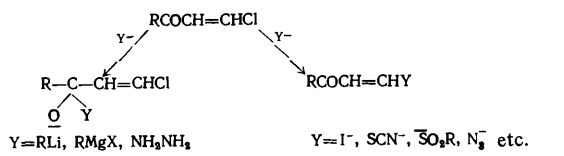
we may examine the interaction of α-halogeno-ketones with various nucleophilic agents[266]:



On the basis of numerous experimental facts, investigators concluded that nucleophilic agents which are at the same time strong bases tend to interact with electrophilic centres having a reduced electron density (for example the carbon atom of C=O group). On the other hand, large readily polarisable anions, which are as a rule weak bases, react preferentially with electrophilic centres having a higher electron density. Jencks and Carriuollo[268] found that, in relation to reactions with a carbonyl carbon atom, the reactivity series of nucleophilic agents is the same as their basicity series. On the other hand, for aliphatic and aromatic electrophilic centres, the reactivity series depends both on the polarisability and on the basicity of the nucleophilic agent and to a greater extent on the polarisability[269]¶. Consequently the presence of two electrophilic centres in the molecules of αβ-unsaturated ketones gives rise to problems of the choice of the ketovinylating agent as a function of the nature of the nucleophilic agent employed. Indeed, the review of all the experimental data concerning the ketovinylation reaction showed that, for example, in the case of β-chlorovinyl ketones there is a distinct tendency for all nucleophilic agents to be classified into two groups. Nucleophilic agents which are very strong bases (RLi, RMgX, NH_2NH_2) react mainly at the carbonyl group (1,2-addition). It is interesting to note that the hydride hydrogen from $LiAlH_4$, $NaBH_4$, and $Al(iso\text{-}OC_3H_7)_3$, which is a very powerful nucleophilic agent, also reacts at the carbonyl group with formation of the corresponding carbinols[163,185,270-272]:



Therefore, with rare exceptions, β-chlorovinyl ketones cannot be used for the ketovinylation of the hydride ion. On the other hand, nucleophilic agents such as the readily polarisable ions RS^-, I^-, SCN^-, N_3^-, $\bar{S}O_2R$, etc., which are weak bases, attack β-chlorovinyl ketones at the β-carbon atom of the double bond. This leads to substitution products (ketovinylation reaction). Hydroxylamine occupies an intermediate position between these two groups, since it reacts in both ways simultaneously:

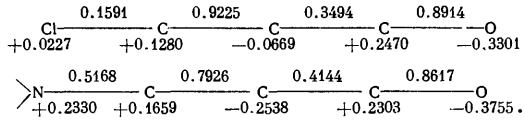


¶ The polarisability and basicity are known not to vary in parallel[269].

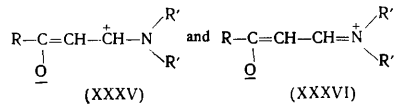
Instead of the sparingly water-soluble β-chlorovinyl ketones, it is very convenient to employ quaternary ammonium salts obtained from them for the ketovinylation of nucleophilic agents of the second type (SO_3^{2-}, CN^-, SO_2R, NO_2^-, CH_3COO^-, etc.). The high electrophilicity of the double bond and solubility in water make these ketovinylating agents very suitable for reactions with anions[34]. In addition, it is important to note that, when quaternary ammonium salts are used, it is possible to achieve the ketovinylation of CN^-,[66] NO_2^-,[150,212] SO_3^{2-},[22] and CH_3COO^- [151] ions, whereas β-chlorovinyl ketones proved to be altogether unsuitable in these cases.

The development of ketovinylation methods made possible the successful application of nucleophilic agents of the first type (RLi, RMgX, NH_2NH_2). It was found that β-dialkylaminovinyl ketones can be usefully employed in reactions with these nucleophilic agents. As a result of the replacement of the chlorine atom by the dimethylamino-group, only powerful nucleophilic agents react with β-dimethylaminovinyl ketones and only at the β-carbon atom of the double bond. In order to account for this sharp change in the properties of the molecule, the following arguments may be put forward. The unshared electron pair of the nitrogen atom very markedly suppresses the electrophilicity of the carbonyl carbon atom. The molecular diagram† of β-aminovinyl ketone shows that the positive charge on the nitrogen atom is larger than the charge on the carbonyl carbon atom.

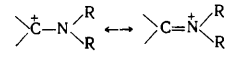
Molecular diagrams of β-chloro- and β-amino-vinyl ketones



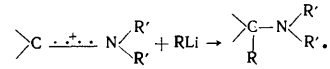
Furthermore, the carbon atom adjacent to the nitrogen also has a large positive charge. Thus structures (XXXV) and (XXXVI) make a considerable contribution to the resonance hybrid of β-aminovinyl ketone, i.e. the groups



characteristic of immonium salts,



are present. In immonium salts the carbon atom adjacent to the nitrogen is attacked by the carbanions derived from RLi and RMgX:[275]



† The molecular diagrams of β-chloro- and β-aminovinyl ketones were calculated by N. P. Gambaryan and A. V. Tutkevich by the LCAO-MO method. The following parameters were used in the calculation: $\alpha_O = \alpha + 1.2\beta$, $\alpha_N = \alpha + \beta$, $\beta_{C=O} = 2\beta$, and $\beta_{CN} = 0.9\beta$;[273] $\alpha_{Cl} = \alpha + 2\beta$ and $\beta_{C-Cl} = 0.4\beta$.[274]

On the other hand, comparison of the molecular diagrams of β-amino- and β-chloro-vinyl ketones shows that the bond order in the C=O group in β-aminovinyl ketones is lower than in the carbonyl group of β-chlorovinyl ketones. Consequently the capacity of the C=O group to undergo addition reactions is much lower in the case of β-aminovinyl ketones. These considerations explain the mode of attack by nucleophilic agents.

It is also clear why β-aminovinyl ketones are passive in relation to weak nucleophilic agents. Indeed, the attack by the nucleophilic agent (Y^-) on the double bond of β-amino- and β-chloro-vinyl ketones leads to the formation of the carbanions RCOĊHCHXY [where X = Cl or $N(CH_3)_2$], in which the electron pairs of the hetero atom X are not conjugated. According to calculation, the gain in conjugation energy in the amino-derivative is higher by 0.42β than in β-chlorovinyl ketones.

Finally, in choosing the ketovinylating agent one should also take into account the possible reaction mechanism. In Section IV, the question of the possible ketovinylation mechanisms will be discussed separately.

IV. STEREOCHEMISTRY AND MECHANISM OF REACTION

The first systematic studies on and the interest in ketovinylation reactions arose in connection with the attempt by Nesmeyanov and coworkers to elucidate nucleophilic substitution at the olefin carbon atom after Nesmeyanov and Borisov[276-278] formulated the rule concerning the retention of configuration in electrophilic and homolytic substitution at an unsaturated reaction centre.

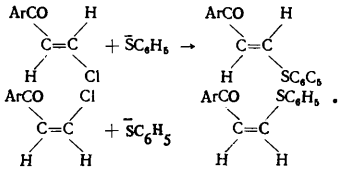
However, the difficulties encountered in the attempt to isolate pure *cis*- and *trans*-isomers of β-substituted vinyl ketones and at the same time the lack of reliable methods for the determination of their configuration directed these studies into the synthetic field.

The mechanism of ketovinylation reactions has so far been little investigated. It has been established in a number of instances that these reactions are bimolecular. Kudryavtseva et al.[279,280] found that the reactions of *trans*-β-chlorovinyl ketones with sodium ethoxide in alcohol are of the second order. However, the stereochemistry of ketovinylation could not be investigated in this model reaction, since the process does not stop at the first stage, a further alcohol molecule adding to the double bond. The kinetics of the reaction of nitrovinyl phenyl ketone with methanol have been studied: one of the pathways in this reaction constitutes ketovinylation[28].

Marchetti and Passalacque[282] found that the reaction of *trans*-β-arylaminovinyl phenyl ketones with pyrrolidine is also a second-order process. It was noted that the configuration is retained during ketovinylation, but this study is likewise restricted to the *trans*-series only.

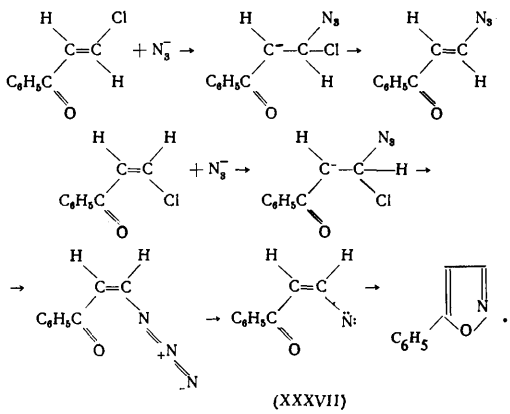
The conclusion that the configuration is retained on substitution in the *trans*-series was based on numerous examples of ketovinylation of nucleophilic agents such as, for example, ferrocenyl-lithium, sodium cyclopentadienide, alkali metal cyanides, potassium phthalimide, sodium nitrite, sulphite, sulphide, and benzenesulphinate, salts containing the complex anions $[Fe(CO)_2C_5H_5\text{-}\pi]^-$ or pyridinatocobaloxime, etc.

However, the stereochemical result of the reaction in the case of both *cis*- and *trans*-isomers has in fact been studied only in two instances—the ketovinylation of thiophenoxide and azide ions. Landini and Montanary showed in a brief communication[215] that aryl *cis*- and *trans*-β-chlorovinyl ketones react with the thiophenoxide ion, the geometrical configuration being mainly retained:



The stereochemistry of the ketovinylation of the azide ion was studied in greater detail. Nesmeyanov and Rybinskaya found that the stereochemical result of the reaction with the azide ion depends on the nature of the substituent X in the compound $C_6H_5COCH{=}CHX$. Thus *trans*-β-chlorovinyl phenyl ketone reacts with sodium azide in aqueous alcohol with formation of *trans*-β-azidovinyl phenyl ketones[283,284]. Other aryl *trans*-β-chlorovinyl ketones and *trans*-β-acylvinyltrimethylammonium quaternary salts react similarly[283]. In the reaction of *cis*-β-chlorovinyl phenyl ketone with sodium azide, 5-phenylisoxazole was isolated as the main product instead of the expected β-azidovinyl phenyl ketone. The formation of this product is regarded as the result of the spontaneous decomposition of the intermediate *cis*-β-azidovinyl phenyl ketone, which, probably as the result of the nearness of the carbonyl and azide groups, is probably converted with evolution of nitrogen into the nitrene species (XXXVII) having the *cis*-configuration. This species is most likely to be stabilised by the reaction of the nucleophilic oxygen atom of the carbonyl group with the electrophilic centre—the nitrene nitrogen:

Scheme 1



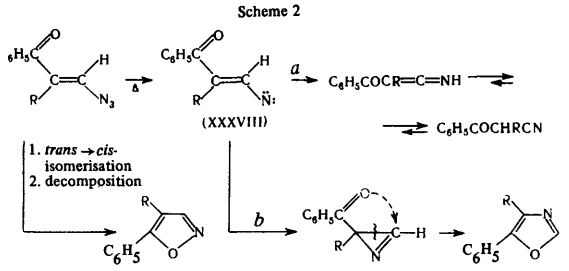
(XXXVII)

In this connection it is interesting to note that benzoisoxazole was obtained from 2-azidobenzophenone, which is known to be a "*cis*-compound"[285].

The configuration of *trans*-β-azidovinyl phenyl ketone was confirmed by spectroscopic and chemical correlation methods[284]. It was found that, when this compound is decomposed by heating in DPA solution, the product is mainly benzoylacetonitrile, 5-phenyloxazole also being isolated in a low yield. Its isomer, 5-phenylisoxazole, was detected only in trace amounts[286]. It may be supposed that the decomposition of *trans*-β-azidovinyl phenyl ketone involves

the formation of the nitrene species (XXXVIII), which has the *trans*-configuration, in contrast to (XXXVII):

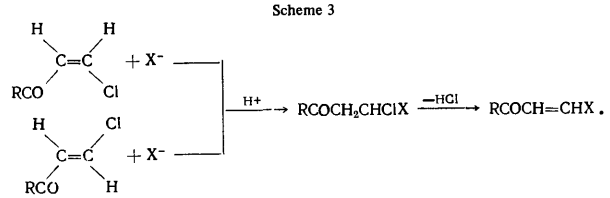
Scheme 2



This species may be stabilised either by rearrangement to the imine of benzoylketen, which is a tautomeric form of benzoylacetonitrile (branch *a* of Scheme 2) or by the formation of the azirine ring, which is known to form readily in the thermolysis of certain vinyl azides[287,288]. The subsequent dissociation of the bond (previously the double bond) with ring closure, as shown in Scheme 2 (branch *b*), leads to the corresponding oxazole. The traces of 5-phenylisoxazole are probably formed as the result of a possible *trans*-*cis*-isomerisation (branch *c*). Consequently the products of the decomposition and subsequent rearrangement differ significantly for *cis*- and *trans*-β-azidovinyl phenyl ketones, which makes it possible to establish the configuration of the products of the ketovinylation of the azide ion. Investigation showed that the ketovinylation of the azide ion with *cis*- and *trans*-β-chlorovinyl phenyl ketones takes place mainly with the retention of the initial geometrical configuration, although it should be noted that in the case of the *cis*-isomer an admixture of *trans*-β-azidovinyl phenyl ketone was isolated as an impurity together with the main product—5-phenylisoxazole.

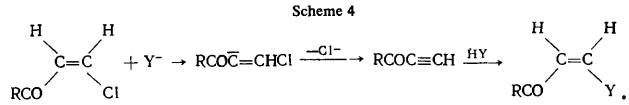
The observed stereochemical results are most consistent with the direct nucleophilic substitution mechanism shown in Scheme 1. The alternative addition—elimination mechanism (Scheme 3), in which the stereochemical result of the reaction should be independent of the configuration of the initial ethylenes, must be rejected on the basis of these results.

Scheme 3

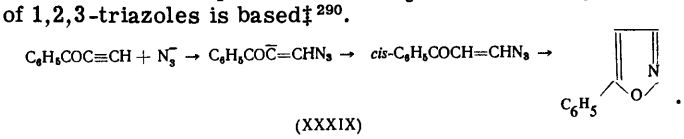


However, it is known that the preferential retention of the initial geometrical configuration in the reaction of the *cis*-isomer is not by itself evidence of the direct nucleophilic substitution mechanism being the only one possible, since the same stereochemical results may be obtained also in the elimination–addition mechanism (Scheme 4).

Scheme 4

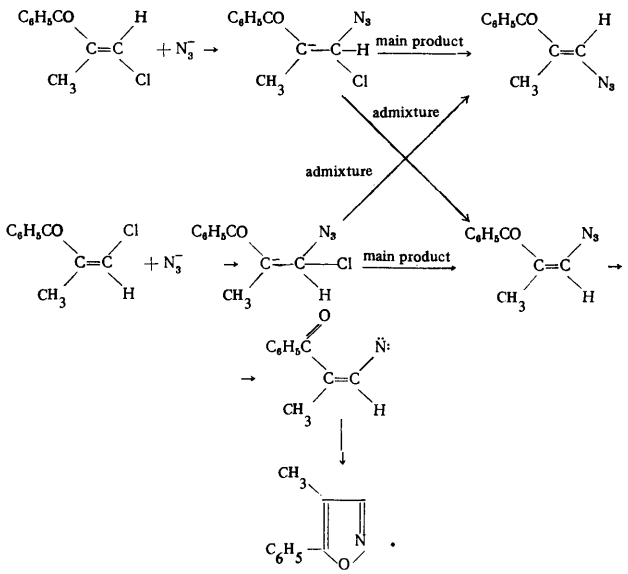


Indeed, on addition of HN_3 to ethynyl ketones at low pH in aqueous solution, 5-phenylisoxazole was obtained[289]. In this connection it is interesting to note that the behaviour of ethynyl ketones in relation to HN_3 differs from the usual reactions of the triple bond with HN_3 on which the synthesis of 1,2,3-triazoles is based‡[290].

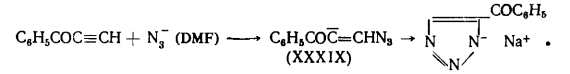


(XXXIX)

In order to exclude the possibility of the elimination–addition mechanism, the stereochemistry of the ketovinylation of the azide ions with both *cis*- and *trans*-α-methyl-substituted β-chlorovinyl phenyl ketones was studied. Since such compounds are much less reactive than the β-chlorovinyl ketones unsubstituted at the carbon atoms of the double bond, dimethylformamide, the nucleophilicity of anions in which is greatly enhanced, was employed as the solvent. Then *trans*-β-chloro-α-methylvinyl phenyl ketone reacted with the N_3^- ion very readily and *trans*-β-azido-α-methylvinyl phenyl ketone was isolated from the nitrogen-containing products. 4-Methyl-5-phenylisoxazole was isolated as an impurity. At the same time, the *cis*-isomer reacted more slowly under the same conditions and 4-methyl-5-phenylisoxazole was isolated from the reaction mixture as the main product; *trans*-β-azido-α-methylvinyl phenyl ketone was isolated as an impurity. Thus, although the elimination–addition mechanism is impossible in such cases (α-hydrogen atoms are absent from the starting materials), substitution products were obtained from both isomers and mainly with retention of the geometrical configuration.



‡ The synthesis of 4-acyl-1,2,3-triazoles on the basis of ethynyl ketones and sodium azide was developed by Nesmeyanov and Rybinskaya using as the medium the aprotic dipolar solvent dimethylformamide[291]:



The sharp difference in the behaviour of ethynyl ketones in relation to azide ions in a proton-containing medium and in dimethylformamide was attributed to different conditions of the stabilisation of the intermediate carbanion (XXXIX), which is very rapidly protonated in the first case with formation of *cis*-β-azidovinyl phenyl ketone (subsequently converted into 5-phenylisoxazole). In dimethylformamide this carbanion can be stabilised only by dipolar cyclisation, which leads to the formation of the stable anion of 4-acyl-1,2,3-triazole.

This shows that in the case considered the direct nucleophilic substitution mechanism probably operates. Recent kinetic data[300] also confirmed this mechanism.

It is interesting to note that, in contrast to unsubstituted *trans*-β-azidovinyl phenyl ketone, the *trans*-β-azido-α-methylvinyl phenyl ketone obtained decomposes on heating with formation of 4-methyl-5-phenyloxazole as the main product and the corresponding benzoylacetonitrile is obtained as an impurity (Scheme 2, branch *b*)[286]. Probably the stabilisation of the nitrene species is influenced not only by stereochemical factors but also by electronic factors. The appearance of the electron-donor CH_3 group adjacent to the double bond facilitates the interaction of the electrophilic nitrene nitrogen atom with the carbon atom of the ethylene bond, which results in the formation of the azirine ring. The conversion of acylazirines into oxazole rings has already been discussed (see p. 449).

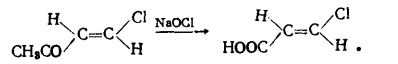
It was found that the stereochemical result of the nucleophilic substitution at the double bond depends on the nature of the group eliminated[292]. In relation to the ketovinylation of the azide ion in proton containing media, the compounds $C_6H_5COCH{=}CHX$ can be divided into several groups.

Compounds of group I, where X = Cl§, Br, $\overset{+}{N}(CH_3)_2$, or NO_2, react with formation of a substitution product, the initial geometrical configuration being largely retained. Compounds where X = $SO_2C_6H_5$ (intermediate group) react with azide ions also forming a substitution product, but in this case the same mixture of substitution products, containing mainly the thermodynamically more stable *trans*-isomer, was obtained regardless of the initial configuration of the substrate. Finally, the reaction of compounds having X = CN or SO_3^- (group II) with the N_3^- ion yielded 4-benzoyl-1,2,3-triazole instead of the substitution product regardless of the initial configuration. As the compounds of both groups contain both powerful [NH_2 and $(CH_3)_3N^+$ in group I and CN in group II] and weak (Cl and Br in group I and SO_3^- in group II) electron acceptors, these observations could not be explained by any electronic effects in the initial molecules. The reasons for the differences in the behaviour of the compounds $C_6H_5COCH{=}CHX$ may be due to the different rates of heterolysis of the C–X bond in the intermediate carbanion $C_6H_5\bar{C}OCH{-}CHXN_3$. If the heterolysis of the C–X bond in this carbanion is fast (group I), or is almost simultaneous with the formation of a new C–N_3 bond, a substitution product with retention on the initial configuration is formed. If the heterolysis of the C–X bond is slower (the intermediate case with X = $SO_2C_6H_5$), the lifetime of such a carbanion is longer and consequently there appears the possibility of free rotation about the single bond in the carbanion. Then of course the thermodynamically more stable substitution product, i.e. *trans*-β-azidovinyl phenyl ketone, is formed with both the *cis*- and *trans*-isomers. Finally, if the heterolysis of the C–X bond is altogether slow, the lifetime of the intermediate carbanion is fairly long and, as a result, there is sufficient time for dipolar cyclisation to occur, i.e. substitution is complicated by cyclisation. This leads to the formation of the triazoline anion, which is converted into the stable heterocyclic 1,2,3-triazole system with elimination of the X^- anion. This classification of eliminated groups in terms of the rate of heterolysis of the C–X bond in the intermediate carbanion into readily and slowly eliminated is supported by the following experimental data. In fact, the chloro- and nitro-groups in β-chloro- or β-nitro-vinyl ketones are substituted by the methoxide anion¶ so fast that it is possible to isolate only the substitution product, while in the case of β-cyanovinyl phenyl ketone the isolation of the addition product $C_6H_5COCH_2CHCN(OCH_3)$ presents no difficulty[294].

V. SYNTHESIS OF GEOMETRICAL ISOMERS OF β-CHLOROVINYL KETONES AND DETERMINATION OF THEIR CONFIGURATION AND CONFORMATION

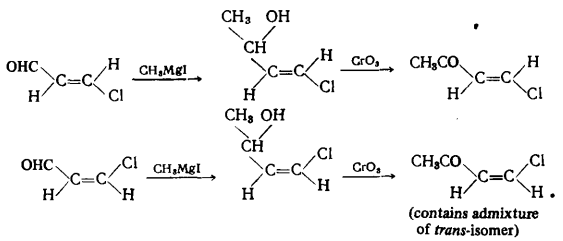
The principal information about the mechanism of nucleophilic substitution at the double bond comes from stereochemical studies. Such data can of course be reliable only if the geometrical configuration of the starting materials and reaction products has been correctly established.

Depending on the method of synthesis, β-chlorovinyl ketones with a definite configuration are obtained as a rule. These methods have been discussed in detail in reviews[1,5-8] and here we shall consider only some of them. The problem of the configuration of β-chlorovinyl ketones obtained by the addition of acid chlorides to acetylene in the presence of aluminium chloride was considered for the first time by Kochetkov et al.[295] It was found that the compounds thus obtained belong to the *trans*-series, since the oxidation of β-chlorovinyl methyl ketone with sodium hypochlorite yielded *trans*-β-chloroacrylic acid:



A detailed study of the infrared[10,173], ultraviolet[173], and nuclear magnetic resonance[173] spectra showed that all β-chlorovinyl ketones obtained in this way belong to the *trans*-series.

Skoldinov et al.[17] developed another version of the synthesis of β-chlorovinyl ketones, whereby both *trans*- and *cis*-isomers can be prepared:



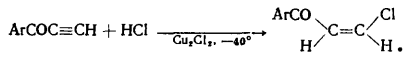
The configuration of the reaction products was established very convincingly by infrared and nuclear magnetic resonance spectroscopy[17,296] and by chemical correlations. However, it was impossible to obtain pure *cis*-β-chlorovinyl methyl ketone by this procedure. According to NMR spectra, the reaction product in this case contained about 30% of the *trans*-isomer[296].

The determination of the configuration of alkyl β-chlorovinyl ketones usually does not present special difficulties. The most important information in these cases was obtained with the aid of infrared and NMR spectra and by chemical correlations. However, Nesmeyanov et al.[259] showed that NMR spectra of aryl β-chlorovinyl ketones of the *trans*-series, susceptible to interpretation, could be

§ Reactions of both *cis*- and *trans*-isomers were investigated with X = Cl.

¶ Both carbon atoms of the ethylene bond in β-nitrovinyl ketones react with $\bar{O}CH_3$. Here we are considering only the attack by $\bar{O}CH_3$ on the β-carbon atom. The problem of the mode of addition of nucleophilic agents to the system XCH=CHY was examined by Nesmeyanov et al.[293]

obtained only with a 100 MHz instrument, since the characteristic AB quartet of the protons at the double bond is partially overlapped by signals due to the protons of the aromatic ring. Aryl *cis*-β-chlorovinyl ketones were obtained by the addition of hydrogen chlorides to aryl ethynyl ketones in the presence of copper(I) chloride[215]:



Their configuration was established by the absence of absorption in their spectra at 930–940 cm^{-1} and on the basis of NMR spectra[284]. In this case the interpretation of the NMR spectrum was extremely simple.

The study of the properties of the *cis*- and *trans*-isomers of aryl β-chlorovinyl ketones[215,284] showed that the *trans*-form is thermodynamically more stable, while the *cis*-isomers are extremely labile and are readily converted into *trans*-isomers under the action of hydrogen chloride even at room temperature. Therefore in their synthesis from ethynyl ketones and hydrogen chloride it is necessary to employ an exactly calculated amount of hydrogen chloride and the reaction temperature should not exceed −40°C. It is noteworthy that *cis*-β-chlorovinyl methyl ketone also proved to be less stable than the *trans*-isomer[17]. The lower stability of the *cis*-isomers can probably be accounted for by the steric interaction between the RCO and Cl groups located close together, in which dipole–dipole repulsion may play a major role[17]. *trans*-β-Chloro-α-methylvinyl phenyl ketone was synthesised using the Claisen method by the formulation of propiophenone with subsequent treatment of the intermediate β-hydroxy-α-methylvinyl phenyl ketone with thionyl chloride in benzene[284].

According to thin-layer chromatographic and NMR spectroscopic data, the product of this reaction contained an insignificant amount (about 5%) of the *cis*-isomer. The content of the *cis*-isomer may be increased by keeping an ethereal solution of *trans*-β-chloro-α-methylvinyl phenyl ketone in diffuse sunlight. The pure *cis*-isomer was isolated from the mixture by means of preparative thin-layer chromatography. However, the most convenient method for the separation of the isomer proved to be a chemical procedure based on the fact that the *trans*-isomer reacts with sodium sulphite in dimethylformamide much faster than the *cis*-isomer[34]. The configuration of α-methyl-substituted β-chlorovinyl phenyl ketones was established on the basis of NMR spectroscopic data and chemical correlations[284], since neither infrared nor ultraviolet spectra provided adequate information.

Conformational analysis of β-chlorovinyl ketones has been carried in a very limited number of cases. For a simpler model, for example acrolein, it has been shown that the transoid conformation is more stable by approximately 2 kcal $mole^{-1}$ than the cisoid conformation[297]. However, in other αβ-unsaturated carbonyl compounds the relative stabilities of S-*cis*- and S-*trans*-forms are strongly influenced by the dimensions and nature of the substituents. The solvent probably also plays a significant role. One may suppose *a priori* that resonance stabilisation with participation of canonical structures of the type $\overset{+}{Cl}=C-C=C-\bar{O}$ plays an appreciable role in β-chlorovinyl ketones[298]. Benson and Pohland[173], who investigated the infrared and ultraviolet spectra of alkyl *trans*-β-chlorovinyl ketones, attributed the transoid conformation to these compounds. In the study of the infrared and quadrupole resonance spectra of *trans*-β-chlorovinyl methyl ketone and its deuterated derivatives on instruments with a high resolving power, Dabrowski and Terpiński[299] concluded that *trans*-β-chlorovinyl methyl ketone exists in both conformations, S-*cis* and S-*trans*, and that the equilibrium S-*cis* ⇌ S-*trans* is displaced to the right in more polar solvents (CH_3CN, CH_3OH) and conversely to the left in non-polar solvents (carbon tetrachloride, hydrocarbons). This problem has also been discussed by Shapet'ko et al.[296] In the conformational analysis of the *cis*- and *trans*-isomers of β-chloroacrolein and β-chlorovinyl methyl ketone they used the nuclear magnetic resonance spectra of carbon tetrachloride solutions. For comparison, a study was made of the spectra of malonic and methylmalonic dialdehydes, which form cyclic enolic forms and consequently have the cisoid conformation. Analysis of the changes in the chemical shifts of the individual protons in the isomeric transition from the *cis*- to the *trans*-configuration is evidence, according to the authors[296], in favour of the cisoid conformation of both isomers of β-chlorovinyl methyl ketone. Unfortunately, in this case the effect of solvents on conformation was not studied specially, so that the data obtained cannot be fully compared with those of Dybrowski and Terpiński[299], but it should be noted that both groups of investigators concluded that the conformation of *trans*-β-chlorovinyl methyl ketone in carbon tetrachloride solution is predominantly cisoid. This is probably because in a non-polar solvent there is a possibility of direct interaction in the molecule (via the field) of oxygen and chlorine atoms which have opposite charges.

In conclusion, we may mention the investigation of the conformation of ββ-dichlorovinyl ketones carried out recently by American workers[298].

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Institute of Organoelemental Compounds,
Zelinskii Institute of
Organic Chemistry,
Moscow

U.D.C. 547.466

Advances in the Asymmetric Synthesis of α-Amino-acids

K.K.Babievskii and V.K.Latov

The review deals with the advances in the asymmetric synthesis of α-amino-acids. Depending on the nature of the asymmetric reactions, the subject matter has been divided into two parts: asymmetric synthesis of α-amino-acids by catalytic hydrogenation and condensation methods of asymmetric synthesis. The principal characteristics of the asyymetric syntheses have been assessed as a function of various factors: the type of catalyst, the structure of the substrates, and the solvent. Much attention has been devoted to theoretical concepts which make it possible to understand the reasons for the occurrence of a new dissymmetric centre and the dependence of its configuration on that of the asymmetrising agent. The bibliography includes 85 references.

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I. INTRODUCTION

The requirement for α-amino-acids is at present very great: their use in biochemistry, food, medicine, etc. is being extended. A number of effective synthetic and microbiological methods have been developed for the preparation of α-amino-acids both on laboratory and industrial scales [1,2]. A disadvantage of the synthetic methods is the formation of optically inactive racemic products. Therefore, despite the existence of many methods for the separation of racemic α-amino-acids into optical isomers [1], synthesis has acquired increasing importance, particularly in recent times [3-5].

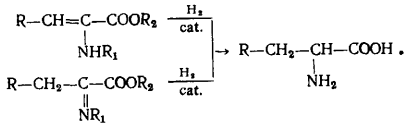
The essential feature of the asymmetric synthesis consists in the generation in the molecule during the reaction under the influence of asymmetrising agents of a new dissymmetric centre with a definite steric configuration. If the asymmetrising agent is an optically active compound, usually eliminated after the formation of the new dissymmetric centre, we are dealing with partial asymmetric synthesis. When a physical asymmetrising factor is employed, for example circularly polarised light, we are dealing with absolute asymmetric synthesis.

While the first successful asymmetric syntheses were achieved as early as the beginning of the present century, the asymmetric synthesis of α-amino-acids began to be investigated systematically only in the last decade. Klabunovskii's monograph [3] published in 1960 described the asymmetric synthesis of α-amino-acids only in general terms, since the bulk of the work on this question was published after 1960. Isolated examples of the asymmetric synthesis of α-amino-acids can be found in books [4,5] dealing with problems of the stereochemistry of organic compounds. These data are supplemented to some extent by the reviews of Mitsui dealing with asymmetric synthesis [6] and asymmetric hydrogenation [7].

In the present paper studies on the asymmetric synthesis of α-amino-acids published up to 1968 are reviewed. In the assessment of the results of asymmetric synthesis the authors endeavoured as far as possible to describe its principal characteristic: the yield of the main product and its optical purity or degree of asymmetric synthesis. Much attention has been devoted to theoretical concepts which explain the relation between the configurations of the new dissymmetric centre and the asymmetrising agent.

II. ASYMMETRIC HYDROGENATION OF DOUBLE BONDS

One of the main methods for the asymmetric synthesis of α-amino-acids is the asymmetric hydrogenation of their unsaturated precursors. This group of compounds includes αβ-unsaturated α-amino-acids and the imino-derivatives of α-keto-acids:



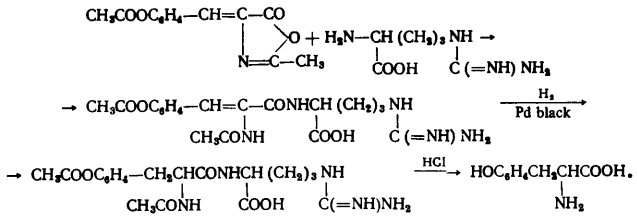
The asymmetric hydrogenation of double bonds results in the formation of an asymmetric α-carbon atom. After the elimination of the groups R_1 and R_2, optically active α-amino-acids are obtained.

The asymmetrising agent in catalytic hydrogenation may be the optically active group R_1 or R_2 forming part of the initial molecule and eliminated after asymmetric hydrogenation or a dissymmetric catalyst may be used. In the latter case the initial molecule does not contain optically active groups.

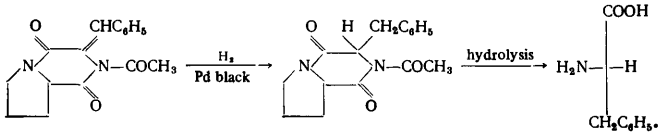
1. Asymmetric Hydrogenation of αβ-Unsaturated α-Amino-acids

The first asymmetric synthesis of an α-amino-acid by catalytic asymmetric hydrogenation was that of D-tyrosine

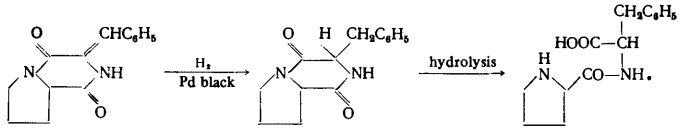
achieved by Bergmann et al.[8] L-Arginine was used as the asymmetrising agent. The hydrogenation over palladium black of the unsaturated peptide of α-acetamido-*p*-acetoxycinnamic acid and L-arginine resulted in the preferential formation of diacetyl-D-tyrosyl-L-arginine. The hydrolysis of the dipeptide in 20% hydrochloric acid yielded D-tyrosine with $[\alpha]_D^{21} = +9.5°$ (4% HCl); for optically pure D-tyrosine, $[\alpha]_D^{20} = +11.8°$:



Somewhat later Bergmann and Tietzmann[9] obtained the dioxopiperazine derivative of *N*-acetyl-L-phenylalanyl-L-proline with $[\alpha]_D^{22} = +202.6°$ in about 50% yield by the reduction of the optically active dioxopiperazine derivative of *N*-acetyldehydrophenylalanyl-L-proline over palladium black. After the hydrolytic elimination of the asymmetrising agent (L-proline), L-phenylalanine with $[\alpha]_D^{27} = -33.9°$ was obtained:

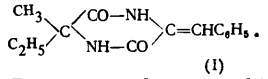


After the hydrogenation of the dioxopiperazine derivative of dehydrophenylalanyl-L-proline over palladium black, the dioxopiperazine derivative of L-phenylalanyl-L-proline was isolated, its hydrolysis in hydrochloric acid giving a 25% yield of pure L-prolyl-L-phenylalanine with $[\alpha]_D^{25} = -40.8°$ (5% in 20% HCl):



Although the initial asymmetrising agent (L-proline) was contained in the resulting dipeptide, nevertheless it can be supposed that L-phenylalanine is formed preferentially during the hydrogenation, since the rotation of the peptide agreed satisfactorily with that of synthetic L-prolyl-L-phenylalanine ($[\alpha]_D^{20} = -40.9$).[10]

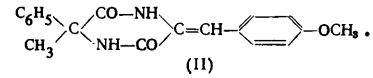
Subsequently, using optically active α-amino-acids as the asymmetrising agents, Akabori and coworkers[11,12] achieved the asymmetric synthesis of phenylalanine. They obtained from the methyl ester of *N*-chloroacetyl-L-isovaline acted upon by ammonia in methanol the dioxopiperazine derived from glycyl-L-isovaline, which in the presence of acetic anhydride at 160°C forms with benzaldehyde the dioxopiperazine derived from dehydrophenylalanyl-L-isovaline (I). Hydrogenation of compound (I) over platinum oxide yields the dioxopiperazine derived from L-phenylalanyl-L-isovaline, from which L-phenylalanine with $[\alpha]_D^{12} = -29°$ was obtained after the hydrolytic elimination of the asymmetrising agent—L-isovaline:



(I)

The corresponding D-compounds were obtained similarly from *N*-chloroacetyl-D-isovaline.

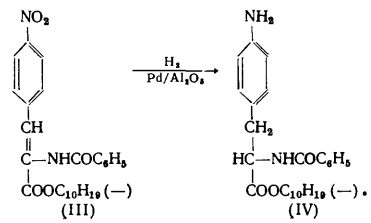
Using the same sequence of reactions, Maeda[13] synthesised optically active L-tyrosine with $[\alpha]_D^{20} = -2.14°$ (20% HCl) by the catalytic hydrogenation over palladium oxide of compound (II) with subsequent hydrolysis of the resulting dioxopiperazine:



(II)

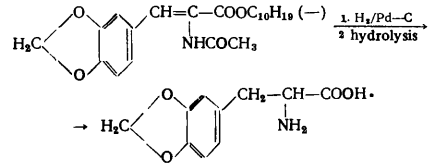
In this case the starting compound and the asymmetrising agent was *N*-chloroacetyl-(+)-α-amino-α-phenylpropionic acid.

Together with optically active amino-acids, optically active menthol has found wide application as an asymmetrising agent. In the hydrogenation of (−)-menthyl esters of α-benzamido-*p*-nitrocinnamic acid (III) over palladium deposited on alumina, Pedrazzoli[14,15] obtained at 60°C a mixture of two diastereoisomeric (−)-menthyl esters of *p*-amino-α-benzamidohydrocinnamic acid containing 30% of the ester (IVa) with $[\alpha]_D = -9°$ (0.5; alcohol) and 60% of the ester (IVb) with $[\alpha]_D = -47.5°$ (0.5; alcohol). After fractional crystallisation, the esters (IVa) and (IVb) were hydrolysed and virtually optically pure D-*p*-aminophenylalanine [from compound (IVa)] with $[\alpha]_D = +45°$ (1.5; water) and L-*p*-aminophenylalanine [from compound (IVb)] with $[\alpha]_D = -42°$ (1.5; water) were obtained:



In order to estimate the degree of asymmetric synthesis achieved in the stage involving the hydrogenation of the ester (III), it is necessary to take into account the relative amounts of the diastereoisomers (IVa) and (IVa). Since the amount of compound (IVb) formed was twice as great as that of compound (IVa), the degree of asymmetric synthesis or the optical yield of the reaction amounts to about 33%. The hydrogenation under the same conditions of the bornyl ester of α-benzamido-*p*-nitrocinnamic acid yielded after one recrystallisation from benzene and subsequent acid hydrolysis virtually inactive *p*-aminophenylalanine with $[\alpha]_D^{25} = +2°$ (1.5; water).

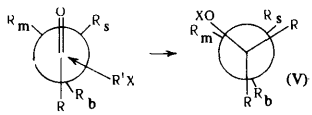
In some cases the isolation of the racemic final product does not alone constitute evidence of the absence of asymmetric synthesis. The isolation of certain α-amino-acids from their derivatives may be accompanied by racemisation. However, if unequal amounts of the diastereoisomers are formed in the hydrogenation stage, asymmetric synthesis still takes place. Thus Yamada et al.[16], who reduced the (−)-menthyl ester of α-acetamido-β-[3,4-methylenedioxyphenyl]acrylic acid in the presence of 10% palladium on charcoal in ethanol and benzene, obtained an excess of the laevorotatory hydrogenation product—an L-alanine derivative, the excess being greater in ethanol than in benzene:



However, both acid and alkaline hydrolysis of the ester was accompanied by almost total racemisation, as a result of which optically inactive 3,4-methylenedioxyphenylalanine was isolated.

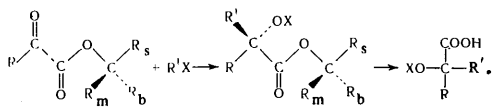
Recently the study of asymmetric syntheses has been based on theoretical concepts whereby it is possible to predict the configuration of the optical isomer formed preferentially. The studies of Cram [17] and Prelog and coworkers [18-21] are important in the development of such concepts, based on the examination of the conformation of molecules.

The investigation of the addition of various reagents, for example hydride hydrogen or organometallic compounds, to the carbonyl group adjacent to the dissymmetric centre, enabled Cram and Abd Elhafez [17] to establish a relation whereby it is possible to predict the configuration of the diastereoisomer formed. The starting material reacts with the reagent R'X in the conformation where the carbonyl oxygen is located between the two smallest substituents and the dissymmetric centre (R_S, R_m, and R_b are small, medium, and big substituents respectively).



The reagent R'X approaches the carbonyl oxygen from the sterically less hindered side, i.e. from the side of the group R_S, which leads to the preferential formation of the compound with the configuration (V). In this case it is possible to observe the maximum influence of the asymmetrising agent, since the centre inducing the asymmetry is directly linked to the dissymmetric centre produced.

Prelog and coworkers [18-21] showed that similar concepts may be used also for systems in which the asymmetrising centre is not located in the immediate vicinity of the dissymmetric centre produced. Thus Prelog examined the stereochemical specificity of the reaction of the α-keto-esters of asymmetric alcohols with Grignard reagents:

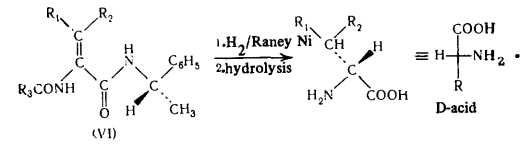


In Prelog's mechanism the α-keto-ester molecule is arbitrarily oriented in such a way that both carbonyl groups are antiparallel and the smallest group R_S of the optically active residue of the alcohol is in the plane of the ester group. Then the reagent R' approaches the ketonic carbonyl group from the side of the medium-size substituent R_m which in fact determines the preferential configuration of the reaction product formed. The reagent can also of course approach the reaction centre from the other, more sterically hindered side, which lowers the optical purity of the product.

Since the reaction products are diastereoisomeric, it may be assumed that the transition states leading to them are also diastereoisomeric and consequently differ in free energy. However, since the initial state in both cases is the same, the activation energies for these reactions are different and the two products are formed at different rates.

Similar ideas can be used also in the study of catalytic asymmetric reactions [20,21]. However, in contrast to homogeneous catalytic syntheses, in asymmetric syntheses in the presence of heterogeneous catalysts such simple relations may be complicated by the orienting effect of the catalyst surface [22].

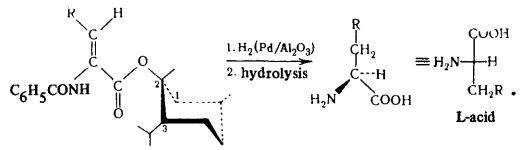
Using the concepts of Cram and Prelog, Sheehan and Chandler [23] were able to predict the configuration of the valine and phenylalanine isomers formed in excess in the hydrogenation of the corresponding optically active methylbenzylamides of α-acetamido-αβ-unsaturated acids over Raney nickel. L-(−)-α-Methylbenzylamine, the L-configuration of which had been established by Leite [24] on the basis of its relation to that of L-alanine, was used as the asymmetrising agent. It was assumed that hydrogen is adsorbed on the surface of the catalyst and that the substrate reaches the catalytic surface from the least hindered side. When L-(−)-α-methylbenzylamine is used, the least hindered side for the substrate (V) will be the region over the plane of the image and consequently the α-amino-acid formed will have the D-configuration.



(VI)

Indeed, in the hydrogenation of L-α-methylbenzylamide of α-acetamido-ββ-dimethylacrylic acid ($R_1 = R_2 = R_3 = CH_3$) followed by the acid hydrolysis of the hydrogenation product, D-valine of 39% optical purity was obtained in 90% yield. The hydrogenation of the corresponding benzoyl derivative ($R_3 = C_6H_5$) also resulted in the formation of D-valine of 18% optical purity in 90% yield. On the other hand, when the D-α-methylbenzylamide of α-benzamido-ββ-dimethylacrylic acid ($R_1 = R_2 = CH_3$; $R_3 = C_6H_5$; asymmetrising agent—D-α-methylbenzylamine) was hydrogenated, the final product was L-valine of 18% optical purity. D-Phenylalanine with an optical yield of 6% (reaction yield 91%) was obtained similarly from L-α-methylbenzylamide of α-benzamidocinnamic acid ($R_1 = R_3 = C_6H_5$; $R_2 = H$).

The preferential formation of L-*p*-aminophenylalanine observed by Pedrazzolli [14,15] can be explained similarly:



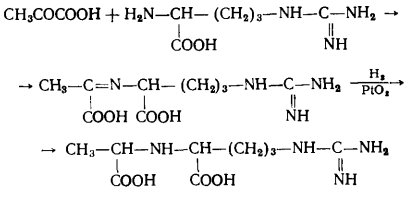
According to Prelog, the (−)-menthyl residue is oriented in such a way that the smallest substituent at the C_2–H atom is screened by the double bond. Of the other two substituents at the C_2 atom, the methylene group of the ring (at C_1) may be regarded as of medium size and the methylidyne group with an isopropyl substituent (C_3) may be regarded as having the maximum size. Consequently hydrogen will attack the double bond preferentially from the least hindered side of the methylene group of the ring (C_1), i.e. from the side opposite to that of the plane of the image. Hence it is clear that an α-amino-acid with the L-configuration should form preferentially.

However, one should bear in mind the possible distortion of the relative amounts of the stereoisomers in the isolation of the reaction product. Therefore in the estimation of the optical yield one should not consider the yield of the optically active substance after isolation but its formation as a result of the reaction. Since in a number of studies [8,9,11-13] the yield of the main reaction product did not exceed 50%, theoretical discussion of these results cannot lead to a reliable interpretation.

2. Asymmetric Hydrogenation of Imino-derivatives of α-Keto-acids

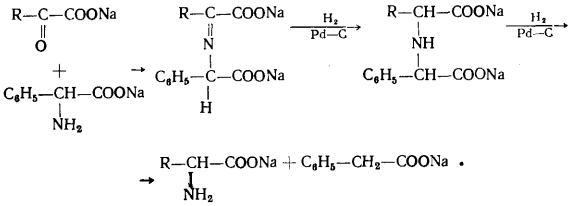
The asymmetric synthesis of α-amino-acids by the catalytic hydrogenation of the imino-derivatives of keto-acids has been most thoroughly investigated. The interest in this reaction is due in the first place to the fact that it constitutes a model of the biochemical transamination of amino-acids in the living organism, which consists in the reversible transfer of the amino-group from the amino-acid to an α-keto-acid without the intermediate formation of ammonia.

In 1939 Knoop and Martius [25] achieved the synthesis of octopine by the reaction of L-arginine with pyruvic acid with simultaneous hydrogenation of the C=N bond over platinum oxide in aqueous solution. The maximum yield of crude octopine reached 85%:



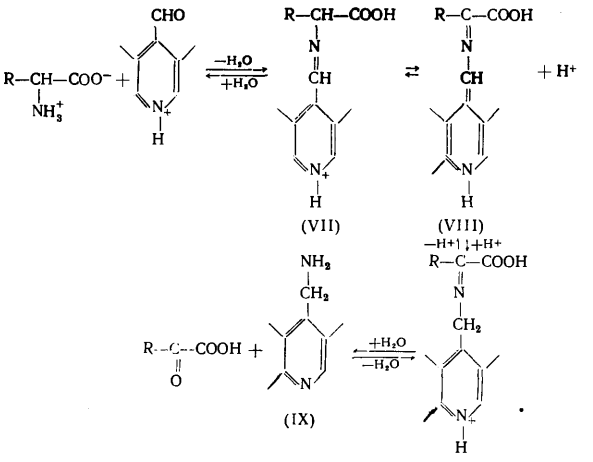
Later Herbst and Swart [26] showed that the product formed in this reaction is iso-octopine—a diastereoisomer of natural octopine containing an alanine residue with the L-configuration. Thus in this case L-arginine induces the formation of a new dissymmetric centre with predominantly the L-configuration.

Recently Harada [27,28] noted that sodium phenylglycinate readily splits into ammonia and phenylacetic acid on hydrogenation in aqueous solution in the presence of palladium or palladium hydroxide on charcoal. Using these data, he achieved a number of asymmetric syntheses, hydrogenating a mixture of sodium D- or L-phenylglycinate with α-keto-acids over the above catalysts in aqueous solution. The reaction probably takes place by the mechanism



In this way he obtained D- and L-alanine with an optical purity of 31–53% in a yield of 28–41%, D- and L-α-amino butyric acids with an optical purity of 24–39% in a yield of 38–41%, and D-glutamic acid with an optical purity of 45–58% in a yield of 25%. It is interesting to note that L-phenylglycine induces the formation of L-amino-acids and D-phenylglycine the formation of D-amino-acids. Harada essentially achieved the reductive asymmetric transamination reaction.

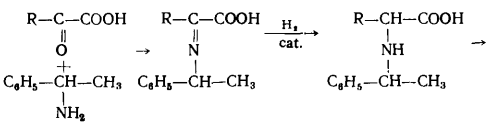
The mechanism of biochemical transamination has been to a considerable degree elucidated and consists in the reductive amination of α-keto-acids by the amino-acid, the process being catalysed by enzymes—amino-transferases. The non-protein component of amino-transferases is pyridoxal phosphate, which plays the role of the agent transferring amino-groups from amino-acids to α-keto-acids [29,30]:

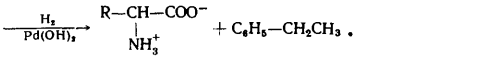


Pyridoxal phosphate forms with the α-amino-acid a Schiff base (VII), from the α-carbon atom of which a proton is readily removed. If the proton adds to the –CH= group of the intermediate (VIII) and then the >C=N– bond is hydrolysed, the final reaction products are an α-keto-acid and pyridoxamine phosphate (IX). The reverse reaction of compound (IX) with the α-keto-acid is a transamination process, the stereochemistry of which is of interest. Enzymes evidently create an asymmetric environment for the strictly stereospecific addition of H to compound (VIII) with formation of compound (VII) and finally of the amino-acid.

However, together with the enzymes, the optically active amino-acid involved in the transamination probably also has an asymmetrising effect. To elucidate this question, Longenecker and Snell [31] carried out the non-enzymic transamination between D- and L-alanine or D- and L-phenylalanine and α-oxoglutaric acid in the presence of a copper(II) complex of pyridoxal. It was found that, regardless of temperature (37–100°C), an excess of glutamic acid with the same configuration as that of the α-amino acid used was always formed, although it did not exceed 10%. Thus 55% of L-glutamic acid and 44.9% of D-glutamic acid was formed when L-phenylalanine was used, while in the presence of D-phenylalanine the yields were 52.7% of D-glutamic acid and 47.3% of L-glutamic acid. When racemic initial amino-acids were employed, racemic glutamic acid was produced. Similar results were obtained also when alanine was the starting material. The data of Longenecker and Snell [31] suggest that in biochemical transamination the main asymmetrising effect is due to enzymes.

Subsequent studies on non-enzymic hydrogenation of optically active imino-derivatives of α-keto-acids demonstrated the possibility of a fairly considerable asymmetrising effect of the optically active component on the stereochemistry of the addition of hydrogen. Hiskey and Northrop [32] used D-(+)- and L-(–)-α-methylbenzylamine as the asymmetrising agent and carried out the hydrogenation according to the following scheme:



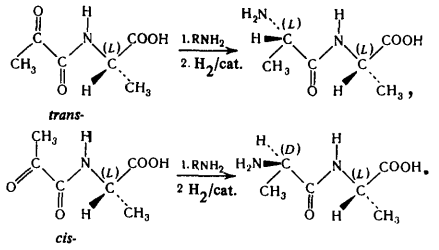


The hydrogenation was performed in the presence of palladium or its hydroxide on charcoal. Optically active alanine, phenylalanine, α-aminobutyric acid, and valine with a high degree of optical purity (56–91%) were obtained in this way. The configuration of the α-amino-acid formed was that of the α-methylbenzylamine employed. The optical purity of the α-amino-acid depended on both the type of catalyst and on the size of the group R in the α-keto acid. In the hydrogenation of the derivative of D-(+)-α-methylbenzylamine and pyruvic acid over the Pd/C catalyst the excess of the D-isomer in the alanine isolated was 85.2% (yield 47.9%), over $Pd(OH)_2/C$ the excess was 91.1% (yield 78%), and over PtO_2 the excess was 56.3% (yield 59.2%). With increase in the bulk of the group R of the α-keto-acid, the hydrogenation becomes less stereospecific: the optical yield of α-amino-acids decreases from 82% for alanine (R = CH_3) to 63% for α-aminobutyric acid (R = CH_2CH_3) and 28% for valine [R = $CH(CH_3)_2$].

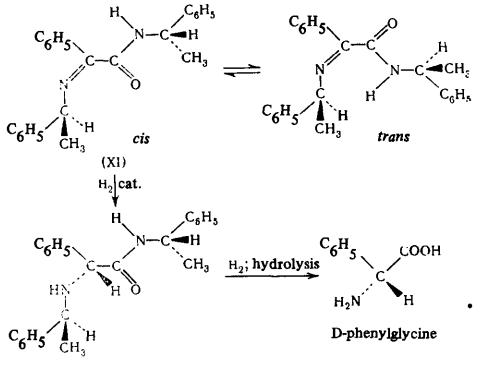
In 1965 Hiskey and Northrop published the results of an interesting investigation [33] in which the asymmetrising role of the amine residue in the azomethine group was assessed. This assessment was achieved by investigating the competing effect of dissymmetric groups at the imino- and carboxy-groups attached to the pyruvic acid residue. For this purpose, the imino-derivatives of *N*-pyruvyl-L-alanine or *N*-pyruvylglycine were hydrogenated together with optically active α-methylbenzylamines. As was to be expected, according to Hiskey and Northrop [32], with *N*-pyruvylglycine, L-(−)- and D-(+)-α-methylbenzylamines lead to the formation of L-alanylglycine (optical yield 53.5%) and D-alanylglycine (optical yield 58%) respectively. The lower optical yield of alanylglycine compared with alanine (82%)[32] or phenylalanine (74%) is attributed by the authors either to an increase in the bulk of the substrate, which leads to a decrease of the stereospecificity of the hydrogenation or to an unfavourable interaction of the catalyst and the substrate due to the presence in the latter of an additional polar group. The second explanation seems more probable, since L-glutamic acid with a relatively low optical yield (35%) was isolated in the hydrogenation of α-oxoglutaric acid (R = CH_2CH_2COOH) in the presence of three equivalents of L-(−)-α-methylbenzylamine. Reductive amination of *N*-pyruvyl-L-alanine in the presence of D-(+)-α-methylbenzylamine led to an excess of D-alanyl-L-alanine (diastereoisomer ratio DL : LL = 74 : 26) and in the presence of L-(−)-α-methylbenzylamine to an excess of L-alanyl-L-alanine (LL : DL = 64 : 36).

This result indicates a more significant asymmetrising effect of the optically active α-methylbenzylimino-group compared with the amino-acid residue at the carboxy-group. To estimate the asymmetrising effect of the L-alanine residue, reductive amination of *N*-pyruvyl-L-alanine was carried out in the presence of benzylamine. An excess of D-alanyl-L-alanine was then obtained (DL : LL = 67 : 33). The authors regard this result as unexpected since, according to Prelog's rule, the L-alanine residue should induce the formation of a new alanine residue with the D-configuration (on the assumption that the carboxy-group is larger than the methyl group).

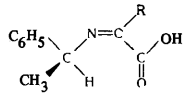
Kanai and Mitsui [34] suggest, however, that in the reductive amination of *N*-pyruvyl-L-alanine the significant factor is the predominant conformation of the substrate. Probably the cisoid conformation predominates, which in fact leads to the formation of D-alanyl-L-alanine:



Kanai and Mitsui arrived at this hypothesis on the basis of the results of the asymmetric hydrogenation of an L-(−)-α-methylbenzylammonium salt (X) and L-(−)-α-methylbenzylamide of L-(−)-α-methylbenzyliminophenylglyoxylic acid (XI) in the presence of the following catalysts: Raney nickel, PtO_2, 5% Pd/C, and 10% $Pd(OH)_2/C$. In the hydrogenation of the salt (X) over $Pd(OH)_2/C$ L-phenylglycine was obtained with an optical yield of 73%, which is similar to the results of Hiskey and Northrop [32]. However, in the hydrogenation of the amide (XI) D-phenylglycine is formed regardless of the type of catalyst. On this basis, Kanai and Mitsui concluded that the predominant conformation of the substrate (XI) is cisoid. It is noteworthy that the optical purity of the D-phenylglycine is low (1–7%).



Harada and Matsumoto [35], who investigated the stereochemistry of the reductive amination of α-keto-acids, believed that the mechanism of Kanai and Mitsui [34] cannot explain the effect of the bulk of the substituents in α-keto-acids on the optical purity of the α-amino-acids formed. Indeed if the substrate molecule were in the cisoid conformation, the substituents R of the α-keto-acids should have scarcely any effect on the mode of addition of hydrogen atoms.

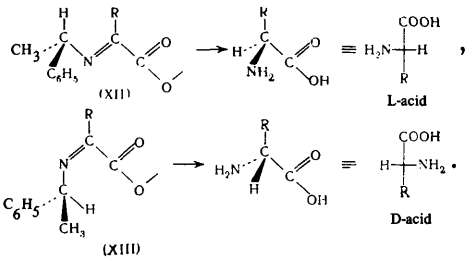


Like Hiskey and Northrop [32], Harada and Matsumoto [35] showed that the optical purity of the α-amino-acid formed decreases with increase in the size of the substituent R:

$$CH_3 > C_2H_5 > C_6H_5 > C_6H_5CH_2 .$$

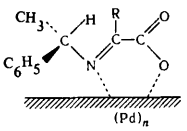
They believe that the most probable conformation of the substrate molecule is the transoid conformation (XII) or

(XIII), the structure (XII) being more probable because of smaller steric hindrance:



The mechanism shows that, when L-α-methylbenzylamine is used, the conformation (XII) leads to the formation of the L-amino-acid, while with the conformation (XIII) the D-amino-acid is formed. As the size of the group R increases, its interaction with the hydrogen atom at the asymmetric carbon atom becomes more pronounced, which may lead to an increase in the fraction of the structure (XIII) and this in turn results in a decrease of the optical purity of the product.

No less important is the examination of the above structures from the standpoint of their capacity to interact with the catalyst. Chang and Hartung [36] believed that such interaction may result in the formation of a rigid cyclic substrate species on the surface of the catalyst. From this point of view, the structure (XII) is to be preferred, since, in contrast to the structure (XIII), it can readily form a five-membered cyclic structure with the catalyst:

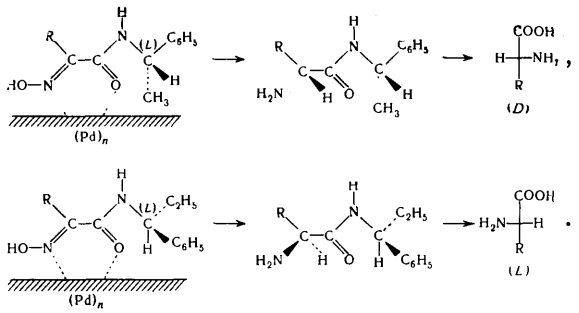


It is readily seen that complex-formation does not lead to a change in the configuration of the α-amino-acid formed.

The replacement of a methyl group by an ethyl group in the optically active alkylbenzylamine [35] leads to a decrease of the optical purity of the hydrogenation products. Prelog established [18,19] that this is caused by a decrease of the difference in the bulk of the substituents at the asymmetric carbon atom of the asymmetrising agent and hence a decrease of the relative steric hindrance to the approach of hydrogen from the two sides of the group >C=N–. This leads to a decrease of the stereospecificity of the hydrogenation and of the optical purity of the α-amino-acids produced.

On the basis of experimental data for the hydrogenation of the oximes of D- and L-α-methylbenzylamide and D- and L-α-ethylbenzylamide of phenylglyoxylic acid and also the Schiff bases formed by benzylamine with the isobutyl esters of *N*-pyruvyl-L-alanine, *N*-pyruvyl-L-valine, and *N*-pyruvyl-D-valine, Harada and Matsumoto [35] gave the most likely explanation of the anomalous synthesis of D-alanyl-L-alanine achieved by Hiskey and Northrop [33].

The hydrogenation of the oximes of L- and D-α-methylbenzylamide of phenylglyoxylic acid led, contrary to Prelog's rule, to the formation of D- and L-phenylglycine respectively. On the other hand, when L- and D-α-ethylbenzylamine were used as the asymmetrising agent, L- and D-phenylglycine were obtained respectively, in agreement with Prelog's rule. Harada and Matsumoto [35] suggest that the substrate molecule is in the cisoid conformation, capable of forming a complex with palladium:

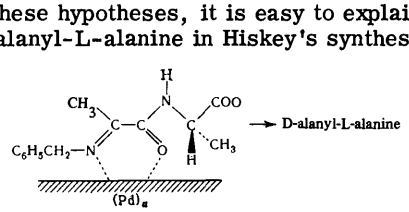


They attribute particular importance to the effect of the catalysts on the conformation of the optically active part of the substrate molecule. The L-α-ethylbenzyl group cannot have the same conformation as the L-α-methylbenzyl group because of the greater bulk of the ethyl group compared with the methyl. Therefore the L-α-ethylbenzyl group rotates with the hydrogen atom, which is least bulky, directed towards the catalyst surface and then the *cis*-addition of hydrogen, occurring on the least hindered side opposite to the plane of the image, leads to the formation of the L-amino-acid.

The hydrogenation of the Schiff bases formed by benzylamine with isobutyl esters of pyruvyl-L-alanine, pyruvyl-L-valine, and pyruvyl-D-valine, which is a closer model of Hiskey's synthesis of D-alanyl-L-alanine, also confirmed these conclusions. When these substrates form complexes with palladium, the methyl group of the alanine derivative and the isopropyl group of the valine derivative lead to different conformations of the asymmetrising agent (in consequence of the different steric hindrance to the interaction with the catalyst surface), exactly as in the preceding case. The Schiff base of the isobutyl ester of pyruvyl-L-alanine gave D-alanyl-L-alanine, while the Schiff bases of the isobutyl esters of pyruvyl-L-valine and pyruvyl-D-valine led to the formation of L-alanyl-L-valine and D-alanyl-D-valine respectively (yield 11–15%, optical purity 32–64%).

The different conformations induced by the groups of the optically active part of the substrate having different sizes (methyl or ethyl, methyl or isopropyl) may be due to the steric hindrance to the interaction between substrate molecules and the catalyst.

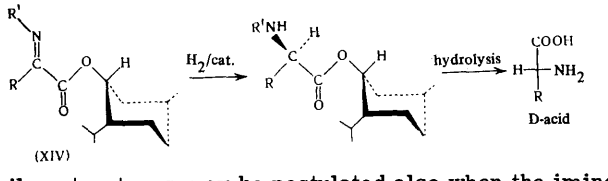
Using these hypotheses, it is easy to explain the formation of D-alanyl-L-alanine in Hiskey's synthesis:



The asymmetric catalytic hydrogenation of (–)-menthyl esters of the imino-derivatives of α-keto-acids was achieved by Matsumoto and Harada [37]. The hydrogenation was carried out over palladium and $Pd(OH)_2$ on charcoal and the amino-acids were isolated by hydrolysing the hydrogenation products in an alkaline medium. D-amino-acids were always obtained from the (–)-menthyl esters of the hydroxyimino- and benzimino-derivatives of pyruvic, α-oxobutyric, and phenylglyoxylic acids, regardless of the type of catalyst employed. The products were D-alanine with an optical purity of 11.0–13.6% and a yield of 67–79%,

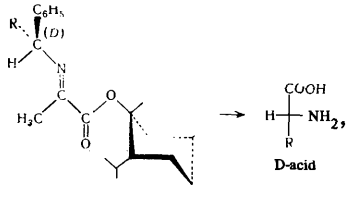
D-aminobutyric acid with an optical purity of 9.44–10.3% and a yield of 62–74%, and D-phenylglycine with an optical purity of 22.7–24.9% (44.2–49.1%)† and a yield of 84–88%. The hydrogenation of the hydroxyimino-derivative led to the formation of the α-amino-acid with a higher optical purity than was obtained with benzimino-derivatives. The type of catalyst employed had virtually no effect on the yield and optical purity of the α-amino-acid, but the benzimino-derivatives of (–)-menthyl esters of pyruvic and α-oxobutyric acids could not be hydrogenated over the Pd/C catalyst. Phenylglycine was synthesised only from the hydroxyimino-derivative of phenylglyoxylic acid, since the benzimino-derivative could not be prepared.

The most interesting results were obtained in the hydrogenation of L-(–)- and D-(+)-α-methylbenzylimino-derivatives of (–)-menthyl pyruvate. The L-(–)-α-methylbenzylimino-derivative gave L-alanine with an optical purity of 16–18% (19–24%) and a yield of 57–62% and the D-(+)-α-methylbenzylimino-derivative gave D-alanine with an optical purity of 56–64% (59–66%) and a yield of 61–67%. If it is remembered that, according to this investigation the (–)-menthyl residue induces the formation of the D-amino acid and according to Hiskey and Northrop [32] the D-(+)-α-methylbenzylimino-residue also induces the formation of the D-acid, then the high optical purity of the D-alanine obtained in the hydrogenation of the D-(+)-α-methylbenzylimino-derivative of (–)-menthyl pyruvate is evidence that the two asymmetrising agents act in accord. On the other hand, the formation of L-alanine in the hydrogenation of the L-(–)-α-methylbenzylimino-derivative of (–)-menthyl pyruvate is evidence of the greater asymmetrising effect of the α-methylbenzylimino-group compared with the (–)-menthyl ester residue, which is consistent with the result of the investigation [33]. The authors explain [37] the steric specificity of the reaction on the basis of the concepts of Cram and Prelog. It is suggested that the most probable structure of the imino-derivative of the (–)-menthyl esters of the α-keto-acid is (XIV). The molecules are adsorbed on the surface of the catalyst from the less hindered side, as a result of which hydrogen atoms will attack the C–N bond from the side opposite to that of the plane of the representation of the mechanism. The products are α-amino-acids with the D-configuration:

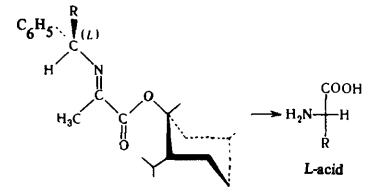


(XIV)

Similar structures may be postulated also when the imino-derivatives of optically active alkylbenzylamines and (–)-menthyl esters of α-keto-acids are employed [35]:



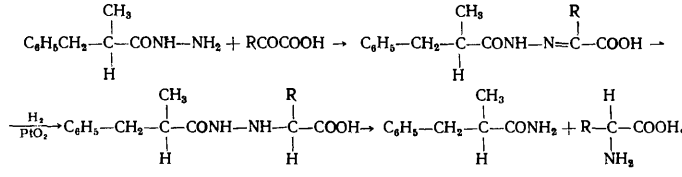
†The figures in brackets indicate, here and subsequently, the optical purity of the amino-acids isolated as the 2,4-dinitrophenyl derivatives.



This mechanism also explains why α-ethylbenzylamine leads to a lower optical purity of the final product than does α-methylbenzylamine.

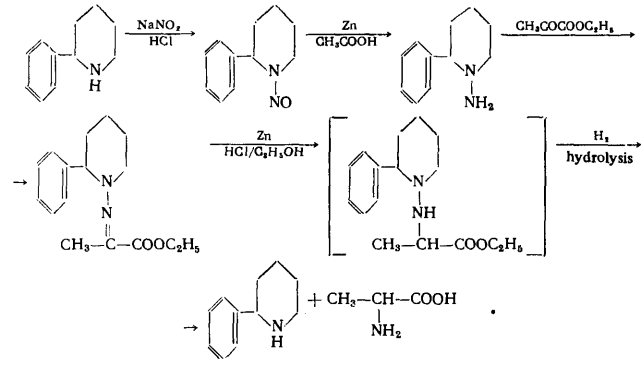
Apart from the asymmetrising agents examined above, such as optically active amino-acids, α-alkylbenzylamines, and (–)-menthol, other optically active substances have also been employed.

Akabori and Sakurai [38] used the optically active hydrazide of D-methylbenzylacetic acid as the asymmetrising agent. The imino-derivatives obtained from the hydrazide and α-keto-acids were hydrogenated over PtO_2 and the optically active α-amino-acids were isolated after the elimination of the asymmetrising agent:



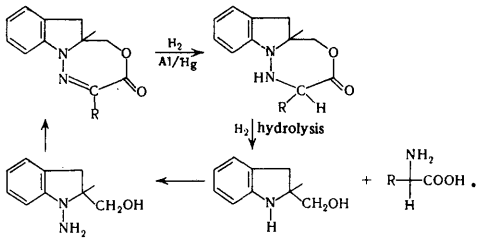
However, the optical yield of the α-amino-acids was low. L-Alanine (R = CH_3) with $[\alpha]_D^{19} = +1.21°$ (8% of asymmetric synthesis) and L-phenylalanine (R = $C_6H_5CH_2$) with $[\alpha]_D^{16} = -1.55°$ (4% of asymmetric synthesis) were obtained in this way.

Kost and coworkers [39,40] used anabasine (the alkaloid of *Anabasis Aphylla*) as the asymmetrising agent. Anabasine was converted into the *N*-amino-compound by nitrosation with subsequent reduction of the nitroso-group. The interaction of *N*-aminoanabasine with ethylpyruvate gave an optically active hydrazone, which was reduced with zinc in alcoholic hydrochloric acid:



This led to the formation in the molecule of a second dissymetric centre. Simultaneously (or subsequently) in the second stage the N–N bond is hydrogenolysed and optically active D-alanine is formed with an optical purity of 40% in a yield of 10%. Despite the low yield of D-alanine (which precludes the conclusion that asymmetric synthesis really takes place), it is noteworthy that the reaction regenerates the asymmetrising agent (anabasine) with virtually the initial (90%) optical activity.

A high optical yield in the synthesis of α-amino-acids was achieved by McCaully [41]. He carried out the asymmetric hydrogenation of an optically active hydrazonolactone with aluminium amalgam with preferential formation of one diastereoisomeric hydrazinolactone. Hydrogenolysis of the hydrazinolactone in an acid medium gives the optically active α-amino-acid and optically active 2-hydroxymethylindoline, which is converted into 1-amino-2-hydroxymethylindoline by nitrosation and subsequent reduction.



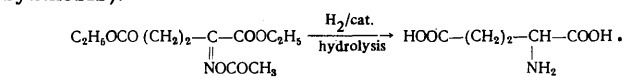
When the last compound is condensed with an α-keto-ester, the hydrazonolactone is formed anew. Optically active alanine (R = CH_3) with an optical yield of 82% and α-aminobutyric acid (R = C_2H_5) with an optical yield of 98% were obtained in this way, the reaction being virtually stereospecific in the second case.

3. Hydrogenation in the Presence of Dissymmetric Catalysts

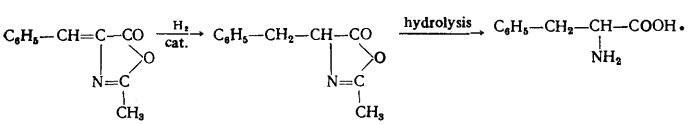
The hydrogenation of unsaturated precursors of α-amino-acids with an optically active asymmetrising group in the initial molecule was described above. This section deals with the formation of optically active α-amino-acids in the hydrogenation of unsaturated optically inactive precursors under the influence of dissymmetric catalysts. Such catalysts are of particular interest, since asymmetric syntheses, analogous to those occurring in the nature under the influence of enzymes, takes place in their presence.

In 1956 Akabori and coworkers [42-44] described the preparation of a dissymmetric heterogeneous catalyst based on the fact that many enzymes (oxidoreductases) are metalproteins. The catalyst, which consisted of a dissymmetric carrier (silk fibroin or acetylfibroin [45]) on which palladium was absorbed, was obtained by reducing the fibroin–$PdCl_2$ complex. The properties of the catalyst were described in detail by Izumi [46-48].

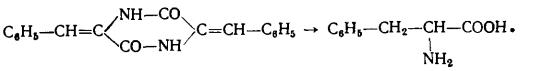
When diethyl α-acetoxyiminoglutarate was reduced over this catalyst at 50°C and 80 atm, optically active L-glutamic acid was formed ($[\alpha]_D^{15}$ = +2.25°, 39% of asymmetric synthesis):



Ethyl α-acetoxyiminophenylpropionate was reduced to D-phenylalanine (yield 25%, optical purity 26.3%) in a similar manner at 70°C and 90 atm. The highest optical purity of D-phenylalanine (35%) was achieved in the hydrogenation under the same conditions of 4-benzylidene-2-methyloxazol-5-one, although the yield of D-phenylalanine was only 6.5%:



D-phenylalanine with the specific rotation $[\alpha]_D^{15}$ = +8.0° was obtained in the hydrogenation of dibenzylidenedioxopiperazine:



The maximum yield (80%) of phenylalanine was achieved in the hydrogenation of α-acetamidocinnamic acid, although the product was inactive.

The study of the infrared spectra of the dissymmetric catalyst [48] showed that, when $PdCl_2$ is adsorbed on silk fibroin, chelate bonds are formed between $PdCl_2$ and fibroin groups such as NH, OH, COOH, and CONH. When the chelate is reduced with hydrogen, the chelate bonds break down and the fibroin resumes its initial structure. The study of X-ray diffraction by the catalyst suggests that part of the palladium in the latter is in the cryptocrystalline state and the remainder assumes the dissymmetric structure of the fibre and this is in fact responsible for the asymmetric synthesis. However, the latest studies suggest that the mechanism of the asymmetrising effect of the dissymmetric catalyst probably consists in the initial asymmetric adsorption of the reactant on the surface of the dissymmetric carrier with subsequent non-stereospecific catalysis [3].

One of the methods developed recently for imparting stereospecificity to optically inactive hydrogenation catalysts consists in their modification with optically active substances—for example α-hydroxy-acids or α-amino-acids. Thus Isoda et al. [49] described a new dissymmetric hydrogenation catalyst based on an amino-acid—palladium and an amino-acid—Raney nickel complex. Best results were achieved when optically active tyrosine was employed. L-Glutamic acid was obtained in this way in the reduction of diethyl α-acetoxyiminoglutarate and D-phenylalanine was synthesised by the reduction of 4-benzylidene-2-methyloxazol-5-one. However, the efficiency of this catalyst was lower than that of palladium on silk fibroin prepared by Akabori and the experimental results were poorly reproducible.

L-Phenylalanine was synthesised similarly by the hydrogenation of α-acetamidocinnamic acid over palladium deposited on charcoal and modified with L-methionine [50].

Studies on catalysts of this type are being vigorously continued at the present time. Best results are obtained with Raney nickel treated with aqueous solutions of optically active substances [51,52]. In the most successful experiments a mixture of methyl α-hydroxybutyrates, consisting of 75% of the L-form and 25% of the D-form was obtained by the hydrogenation of methyl acetoacetate, used as a model compound, over Raney nickel modified with D-tartaric acid.

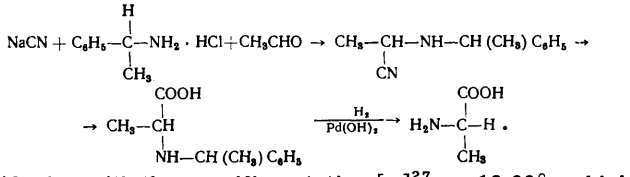
Asymmetric catalytic hydrogenation was achieved in many cases in the presence of optically active substances. Thus Isoda et al. [53] obtained optically active glutamic acid in the hydrogenation of α-hydroxyiminoglutaric acid in the presence of (+)-camphor and (+)-borneol over Raney nickel. Nakazaki [54] achieved the asymmetric hydrogenation of α-acylaminocinnamic acid over Raney nickel in the presence of glucose. After the hydrolysis of the hydrogenation products, optically active D-phenylalanine was isolated with the rotation $[\alpha]_D^{15}$ ranging from +2.22° to 3.58°, depending on the reaction conditions.

In the experiments described above the active substances constitute an optically active medium rather than dissymmetric organic catalysts, since they show no independent catalytic effect.

III. ASYMMETRIC SYNTHESIS OF α-AMINO-ACIDS BY CONDENSATION METHODS

1. The Strecker Synthesis

In 1963 Harada [55] achieved the asymmetric synthesis of alanine by the Strecker reaction. The asymmetrising agent was (−)-α-methylbenzylamine. The synthesis consisted in the interaction of acetaldehyde with HCN or NaCN and (−)-α-methylbenzylamine in methanol at 20°C, the hydrolysis of the resulting aminonitrile to *N*-(α-methylbenzyl)amino-acid, and the elimination of the methylbenzyl group by catalytic hydrogenolysis over $Pd(OH)_2$ by Hiskey's procedure [32]:

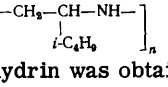


L-Alanine with the specific rotation $[\alpha]_D^{27} = +13.99°$, which corresponds to 95% of asymmetric synthesis, was obtained in this way. Subsequently Harada and Fox [56] carried out this synthesis starting with the previously prepared acetaldehyde cyanohydrin. Depending on the duration of the reaction, L-alanine was obtained with optical purities in the range 86–99% (after one recrystallisation).

The reaction mechanism is still obscure. However, the authors [56] suggest that the most likely cause of the asymmetric synthesis is different rates of the reactions of the D- and L-cyanohydrins with the (−)-amine.

It is believed [57] that this synthesis constitutes a good model of the formation of active α-amino-acids in the prebiological period of the development of the earth.

Interesting results were obtained by Tsuboyama [58] in the cyanohydrin synthesis from benzaldehyde and hydrocyanic acid in benzene in the presence of optically active poly-L-isobutylethyleneimine as the catalyst:

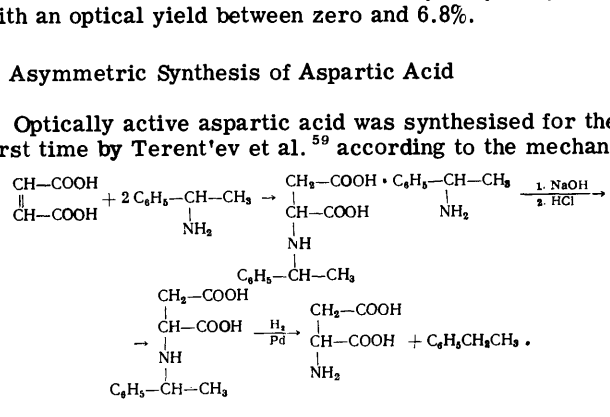


Benzaldehyde cyanohydrin was obtained with an optical yield up to 20%. The asymmetrising effect of the catalyst was attributed by the author to the stereoregularity of the polymer, the presence of dissymmetric centres in the main chain, and the spiral structure of the polymer, which enhances the asymmetrising effect.

The application of styrene–divinylbenzene copolymers containing methyl-α-glucosamine, diethylaminoethylcellulose, and L-leucinol as catalysts of cyanohydrin synthesis led to the formation of benzaldehyde cyanohydrin with an optical yield between zero and 6.8%.

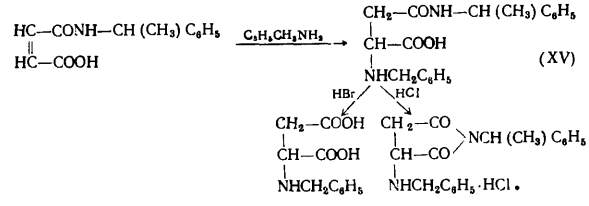
2. Asymmetric Synthesis of Aspartic Acid

Optically active aspartic acid was synthesised for the first time by Terent'ev et al. [59] according to the mechanism



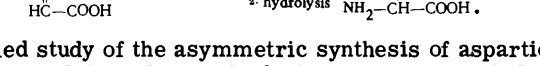
The reaction of maleic acid with (−)-α-methylbenzylamine yields a salt the decomposition of which gives an *N*-substituted aspartic acid. The acid consists of two types of crystals with different solubilities—large, well formed crystals in an amount greater than small crystals combined into spherical pellets. When the large crystals were debenzylated over palladium black, D-aspartic acid with an 88% optical purity was obtained. The small crystals yielded racemic aspartic acid. When (+)-α-methylbenzylamine was employed, two types of crystals were also obtained, in approximately equal amounts. After debenzylation the large crystals gave L-aspartic acid ($[\alpha]_D^{20} = +4.83°$) and the small crystals the racemic acid. The authors [59] suggest that in this case there is either partial asymmetric synthesis or the diastereoisomers are recrystallised.

Livshits and Singerman [60], who repeated Terent'ev's experiment, reject the occurrence of asymmetric synthesis in this process and believe that true asymmetric synthesis of aspartic acid takes place when benzylamine adds to the double bond of poly-(+)-α-methylbenzylamide of maleic acid:



Thin-layer chromatography of the amide (XV) showed the presence of only one substance. Its hydrolysis in a sealed tube at 100°C with 20% hydrochloric acid led to the formation of the imide. On the other hand, when the imide (XV) was refluxed with 48% hydrobromic acid, the product was *N*-benzyl-L-aspartic acid of 60% optical purity, which the authors [61] believe may be debenzylated with complete retention of the configuration.

Subsequently Vlasova [62], who carried out the reaction of mono-(−)-α-methylbenzylamide of maleic acid with ammonia, really achieved the asymmetric synthesis of D-aspartic acid with an optical purity of 80% and a yield of 90%:



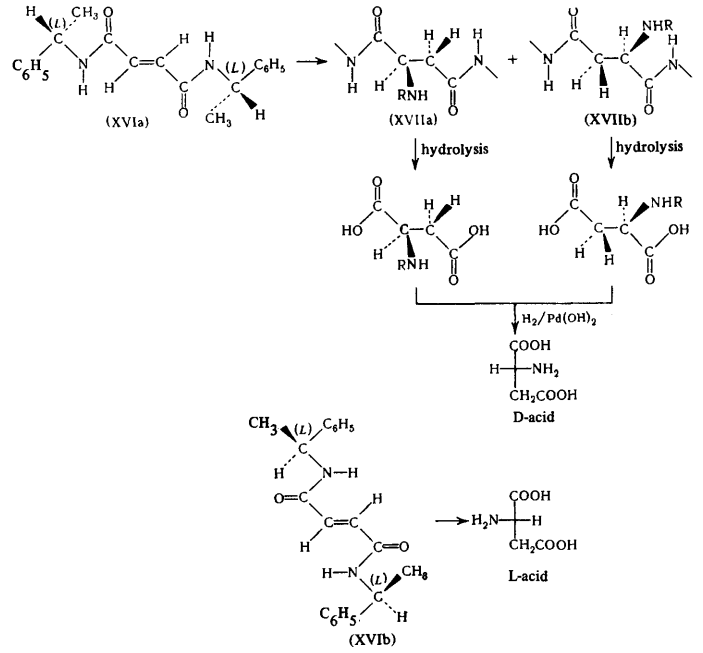
A detailed study of the asymmetric synthesis of aspartic acid from maleic and fumaric derivatives was carried out by Harada and Matsumoto [63]. The following reactions were investigated: (1) the reaction of L-(−)- and D-(+)-α-methylbenzylamine with *NN'*-di-L- and *NN'*-di-D-α-methylbenzylfumaramide (L- and D-fumaramide); (2) the reaction of L-(−)- and D-(+)-α-methylbenzylamine with diethyl maleate and diethyl fumarate. Debenzylation was carried out in the presence of $Pd(OH)_2$ by Hiskey's procedure [32].

The reaction of L-fumaramide with L-(−)-α-methylbenzylamine gave D-aspartic acid with an optical purity of 10.2% (15.3% in the form of the dinitrophenyl derivative) and a yield of 64%. D-Fumaramide and L-(−)-α-methylbenzylamine reacted to form L-aspartic acid with an optical purity of 11.0% (13.7%). The reaction of diethyl maleate with D-(+)-α-methylbenzylamine yielded D-aspartic acid with an optical purity of 12.2% (15.4%) and the reaction with L-(−)-α-methylbenzylamine gave L-aspartic acid. Similarly the interaction of diethyl fumarate with L-(−)-α-methylbenzylamine led to the formation of L-aspartic acid with an optical purity of 7.5% (4.6%) and the interaction with

D-(+)-α-methylbenzylamine gave D-aspartic acid with an optical purity of 6.3%(4.5%).

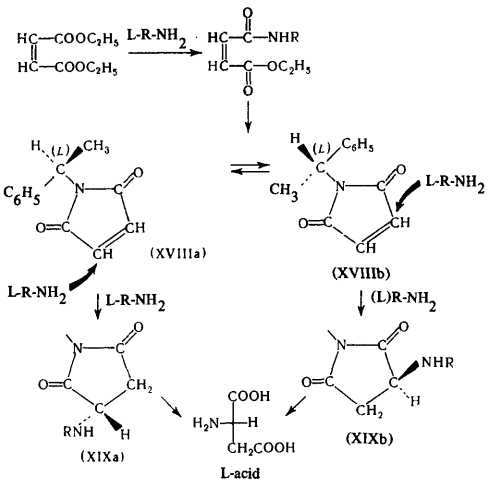
The principal asymmetrising effect in the reaction of L- and D-fumaramide with optically active amines is shown by optically active amide groups. Amides with the L-configuration induce the formation of D-aspartic acid and conversely. The configuration of the amine entering into the reaction apparently does not have a decisive influence on the configuration of the acid formed. Indeed, when optically active amines are replaced by benzylamine, the situation does not change: D- and L-fumaramide yield L- and D-aspartic acid respectively. However, the optical purity of the acids obtained is then lower.

Harada and Matsumoto explained the configuration of the final product on the basis of the hypotheses of Cram and Prelog:

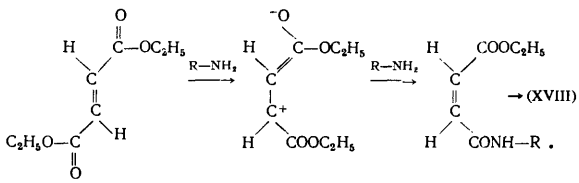


The possible conformations of L-fumaramide are cisoid (XVIa) and transoid (XVIb). The addition of L- or D-α-methylbenzylamine to the double bond of fumaramide in the cisoid conformation takes place preferentially from the least hindered front side of the plane of the image, since both methyl groups are on the reverse side. In this case both addition products, (XVIIa) and (XVIIb), are identical and yield aspartic acid with the D-configuration. The addition of the amine to fumaramide in the transoid conformation (XVIb) leads ultimately to the formation of L-aspartic acid. However the transoid conformation of L-fumaramide (XVIb) is energetically less favourable, since, by virtue of steric hindrance, it cannot be planar. It was shown with the aid of Dreiding stereomodels that in the transoid conformation the distance between the hydrogen of the amide group and the hydrogen at the β-carbon atom is 1.65 Å. Since the van der Waals radius of the hydrogen atom is 1.15 Å, these two hydrogen atoms overlap and prevent the formation of a planar molecule. On the other hand, in the cisoid conformation there is no such steric hindrance and therefore the molecule can form a planar structure.

In the reaction of diethyl maleate and diethyl fumarate with L- or D-α-methylbenzylamine the first stage is the formation of the amides of these acids, which then cyclise to the imide (XVIIIa) or (XVIIIb) as shown below:

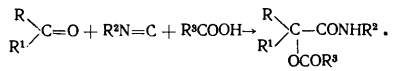


Regardless of the conformation of the *N*-alkylmaleimide (XVIIIa) or (XVIIIb), it is attacked by L-α-methylbenzylamine from the least hindered side (indicated by arrows) forming a derivative of L-aspartic acid. The intermediate addition product—succinimide (XIX)—was isolated as the main reaction product, which confirms this mechanism. Since (XIX) is formed also from diethyl fumarate, Harada and Matsumoto [63] suggested the possibility of the conversion of fumarate into maleate in the reaction



3. Asymmetric Synthesis of α-Amino Acids by the Ugi Reaction‡

As early as 1921 Passerini [67] observed that isonitriles readily condense with carbonyl compounds in the presence of carboxylic acids, forming the amides of α-acyloxy-acids:

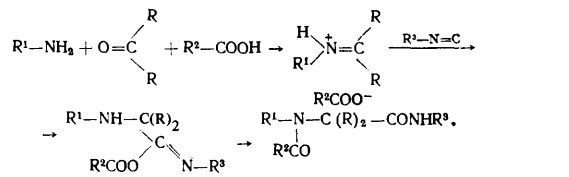


The reaction takes place under very mild conditions (between −20° and +20° C) with almost quantitative yields of the final products [68]. It is noteworthy that the use in the Passerini reaction of an optically active acid leads to the preferential formation of one of the two possible diastereoisomers [69].

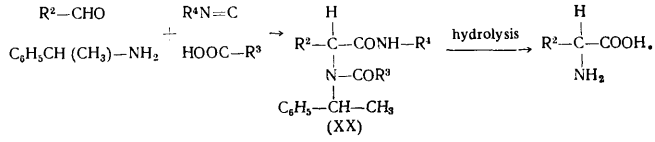
In 1960 Ugi [70] carried out this condensation in the presence of a fourth component (an amine), which led to the discovery of the reaction involving the aminoalkylation of isonitriles by immonium salts, formed from the carbonyl

‡For further details of the reaction, see the reviews of Ugi [64,65] and Gambaryan [66].

compound, the amine, and the acid. The reaction gives under mild conditions almost quantitative yield of the α-amino-acid derivative:



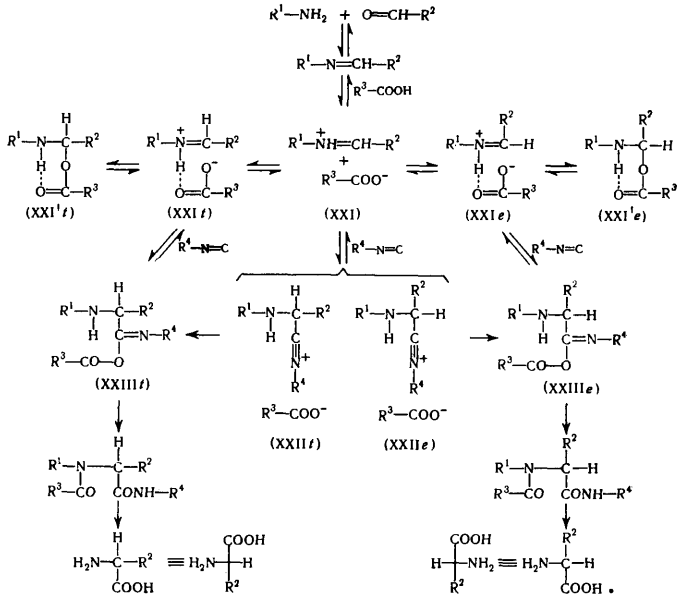
When an optically active amine, for example α-methylbenzylamine, is used, one of the diastereoisomers is formed preferentially and its hydrolysis gives the optically active α-amino-acid [71-73]:



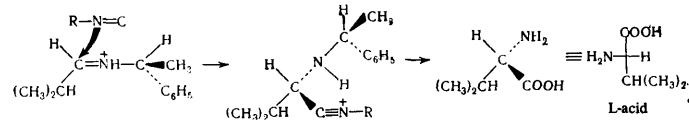
The configuration of the asymmetric carbon atom produced in compound (XX) depends both on the configuration of the asymmetrising agent (the amine) and on the reaction conditions (polarity of the solvent, concentrations of the reactants, and temperature). Thus the interaction of isobutyraldehyde [$R^2 = CH(CH_3)_2$], D-(+)-α-methylbenzylamine, benzoic acid ($R^3 = C_6H_5$), and t-butyl isocyanide [$R^4 = C(CH_3)_3$] at $-70°C$ and about 1 molar reactant concentrations in methanol (conditions *A*) led to the preferential formation of L-valine, while at 0° C and reactant concentrations about 0.1 molar (conditions *B*) D-valine was formed. Similar relations were observed also when other aldehydes, including optically active ones, were employed in the reaction. For example, under conditions *A* the reaction of L-(−)-α-methylbenzylamine, benzoic acid, t-butyl isocyanide, and butyraldehyde ($R^2 = n\text{-}C_3H_7$) or L-(+)-ethylmethylacetaldehyde [$R^2 = L\text{-}CH(CH_3)C_2H_5$] gives D-norvaline or D-alloisoleucine, while under conditions *B* the products are L-norvaline or L-isoleucine respectively. Similarly, when D-(+)-α-methylbenzylamine is employed, the products under conditions *A* are L-norvaline or L-isoleucine and under conditions *B* D-norvaline and D-alloisoleucine respectively. Compounds of type (XX) are usually formed with an optical purity in the range 70–75% and yields of 70–95%; their hydrolysis in hydrochloric acid results in a quantitative yield of the α-amino-acids with the retention of the configuration and optical purity [73].

Thus, when the temperature is reduced and the concentration of the reactant is increased, the configuration opposite to that of the initial amine is induced at the newly formed asymmetric carbon atom, and, conversely, on raising the temperature and lowering the reactant concentration, a compound with the same configuration is formed. The reversal of the configurational relation between the induced and inducing dissymmetric centres as a function of reaction conditions is explained by the fact that the Ugi reaction takes place under different conditions by two stereochemically different mechanisms [72,74-77].

All the reactions of isonitriles, including the Ugi reaction, reduce essentially to electrophilic α-addition of the cationic and anionic centres to the isonitrile carbon atoms. Initially the azomethine derivative is formed from the carbonyl compound and the amine. In a strongly polar medium it is present as a solvated non-oriented ion pair (XXI) with the carboxylic acid. In less polar solvents the azomethine derivatives and the carboxylic acids form hydrogen-bonded diastereoisomeric ion pairs (XXI*t*) and (XXI*e*), which may be in equilibrium with the adducts (XXI′*t*) and (XXI′*e*), where *t* denotes the *threo*-form, i.e. the diastereoisomer in which on direct combination both dissymmetric centres would have the identical configuration, and *e* denotes the *erythro*-form with different configurations of the dissymmetric centres. It is readily seen that the mechanism and stereochemistry of the α-addition of the immonium cation and the carboxylate anion to the isonitrile depend to a high degree on the polarity of the medium. This is either a two-stage process (conditions *B*): (XXI) → (XXII*t*, *e*) → (XXIII*t*, *e*), or a one-stage process (conditions *A*): (XXI*t*, *e*) → (XXIII*t*, *e*):



In strongly polar solvents, for example in ethylene glycol or methanol, at low reactant concentrations and high temperatures the ratio of the products [(XXII*t*): (XXII*e*)] of the addition of the solvated ion pair (XXI) to the isonitrile is determined by steric factors. The *threo*-isomer then forms preferentially, as can be seen in the case of the azomethine derivative obtained from L-(−)-α-methylbenzylamine and isobutyraldehyde:



The two-stage reaction *B* is a kinetically controlled process and the ratio of the reaction products (XXII*t*): : (XXII*e*) is determined by the steric strain of the conformation of the transition state, i.e. depends on the difference between the free energies of the transition states, which, as found for the reaction of L-(−)-α-methylbenzylamine, isobutyraldehyde, benzoic acid, and t-butyl isocyanide, is $\Delta F^{\neq}_{(XXI)\rightarrow(XXII e)} - F^{\neq}_{(XXI)\rightarrow(XXII t)} = 0.71$ kcal mole^{-1}. [74]

In a less polar medium, for example in ethanol and in methanol, at high reactant concentrations or at a low temperature the diastereoisomeric hydrogen-bonded ion pairs

(XXI*t*) and (XXI*e*) formed are in equilibrium, the position of which plays a decisive role in determining the steric course of the process (thermodynamically controlled reaction). Because of the smaller conformational strain, the *erythro*-isomer (XXI*e*) is energetically more favourable and therefore under the given conditions there is preferential formation of α-amino-acids having the configuration opposite to that of the initial amine. If the equilibrium (XXI*t*) ⇌ (XXI*e*) is established rapidly, the ratio of the products of the single-stage reaction A [(XXIII*t*) : (XXIII*e*)] may be determined by the Curtin–Hammett principle. Indeed, for the same reaction of L-(−)-α-methylbenzylamine, isobutyraldehyde, benzoic acid, and t-butyl isocyanide under conditions *A*, we have $\Delta F = F^{\neq}_{(XXI t)\rightarrow(XXIII t)} - F^{\neq}_{(XXI e)\rightarrow(XXIII e)} = 1.02$ kcal mole^{-1}. Evidently the experimental values of $\Delta F^{\neq}$ both for reaction *A* and *B* essentially confirmed the above hypotheses concerning the stereochemistry of these reactions. This concerns of course only the preferential occurrence of the reaction by mechanisms *A* and *B*. However, the high sensitivity of the Ugi reaction to changes in conditions, within the limits of which there is a possibility of controlled synthesis of both L- and D-amino-acid with a high optical purity and yield, makes it one of the most promising synthetic procedures for optically active α-amino-acids.

4. Application of Complexes in the Asymmetric Synthesis of α-Amino-acids

The stereospecificity of coordination compounds in certain reactions is well known[78]. However, only a few papers have been published[79,81,83] on studies where the asymmetrising effect of optically active complexes was employed for the asymmetric synthesis of α-amino-acids. The asymmetric transamination of α-amino-acids in the presence of the copper(II) complex of pyridoxal[31] was mentioned above. It was suggested[31] that a dissymmetric chelate compound is formed and then undergoes stereospecific protonation.

Using the Akabori method[82], Murakami and Takahashi[79–81] achieved the asymmetric synthesis of threonine by the Knoevenagel, reaction involving the condensation of acetaldehyde with the active methylene group of optically active L-[Coen$_2$gly]I$_2$. After the breakdown of the complex reaction products, either optically active threonine with $[\alpha]_D^{13} = +3.84°$ ($c = 2.345$; water) or its 2,4-dinitrophenyl derivative with $[\alpha]_D^{11} = -8.22°$ ($c = 2.34$; 4% aqueous solution of $NaHCO_3$) was isolated. The asymmetric yield of threonine was 8%. Paper chromatography showed that the crude products contained threonine, allothreonine, and glycine in the proportions 7 : 2 : 1.

The condensation of acetaldehyde with glycinatobis-[(−)-propylenediamine]cobalt(III) chloride gave a mixture of threonine, allothreonine, and glycine in the proportions 6.5 : 3 : 0.5. However, the crude threonine in the form of the 2,4-dinitrophenyl derivative (yield 75%) exhibited only weak laevorotation $[\alpha]_D^{11} = -1.2°$ ($c = 5.822$; 4% aqueous solution of $NaHCO_3$). The asymmetric yield of threonine was in this case only about 1%.

Asperger[83] achieved the synthesis of optically active alanine by the coordination of methylaminomalonic acid via both carboxy-groups to the ion (+)-*cis*-α-[Co(LL-αα′-dimethyltriethylenetetramine)Cl$_2$]$^+$ with subsequent decarboxylation of the complex. This gave an alanine complex containing L-alanine with 75% optical purity. However, on liberation from the complex ion and isolation, the L-alanine racemised. Asperger believes that the asymmetrising effect of the complex ion consists in a template action in the coordination of methylaminomalonic acid; the decarboxylation of the optically active complex is stereospecific, leading to the formation of a new dissymmetric centre.

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The studies on the asymmetric synthesis of α-amino-acid examined above demonstrate a rapid increase of interest in this problem. Both asymmetric hydrogenation and condensation methods make it possible to achieve in some cases a high degree of non-enzymic asymmetric synthesis of α-amino-acids. However, systematic studies on this problem are essentially only just beginning and further investigations in this field will be of interest.

So far asymmetric synthesis has been carried out for a restricted number of the simplest α-amino-acids. Therefore it will be very important to develop methods for the asymmetric synthesis of essential α-amino-acids such as tryptophan, lysine, methionine, threonine, etc. The study of the effect of the substrate–catalyst interaction on the optical purity and the configuration of the final product has assumed considerable importance in catalytic asymmetric hydrogenation. The study of the effect of hydrogenation conditions (temperature, pressure, medium) on the degree of asymmetric synthesis is noteworthy, since such conditions can affect not only the magnitude but also the sign of the optical rotation of the hydrogenation products. Interesting results may be obtained in investigations of new types of heterogeneous dissymmetric catalysts. In this connection considerable interest attaches to further investigation of the modification of hydrogenation catalysts by low-molecular optically active substances and also of new complexes of optically active polymers with hydrogenation catalysts, which may serve as models of metal enzymes.

The study of optically active polymers as asymmetrising agents with which the substrate can be linked by bonds of different types—covalent, coordination, salt type, hydrogen bonds, van der Waals forces, electrostatic attraction, etc.—has hardly begun. The progress in synthetic polymer chemistry already permits the preparation of polymeric systems which may serve as simple models of natural enzymes. Probably condensation methods of asymmetric synthesis should yield best results in such systems and much attention must be devoted to the development of such methods. In the study of new procedures for asymmetric synthesis attention must be concentrated on those where the asymmetrising agent is regenerated. Then one may hope that further investigation of the asymmetric synthesis of α-amino-acids and other optically active substances will yield, together with useful practical results, also invaluable information about the nature of enzyme action.

During the preparation of the manuscript for the press several papers on the asymmetric synthesis of α-amino-acids were published. Klabunovskii's monograph[84] contains a number of data on the asymmetric synthesis of α-amino-acids by asymmetric catalytic hydrogenation. The asymmetric synthesis of the monomethyl ester of D-aspartic acid with 98% optical purity is almost stereospecific. It was achieved by Vigneron et al.[85] in the hydrogenation over Raney nickel of the cyclic product of the reaction of (+)-*erythro*-1,2-diphenylethanolamine with dimethyl acetylenedicarboxylate followed by the hydrogenolysis of the reduction product over Pd(OH)$_2$.

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Institute of Organoelemental Compounds, Moscow

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The Chemistry of Quinuclidine

L.N.Yakhontov

The review deals with the chemical properties and the biological activity of the derivatives of 1-azabicyclo[2,2,2] octane widely known as quinuclidine. The work of the Soviet School of Chemists, founded by M.V.Rubtsov, in the field of quinuclidine derivatives is reviewed in detail.
In the review an attempt is made in the first place to examine as a whole the chemistry and the biological action of quinuclidine derivatives from the standpoint of the characteristics of the structure of the quinuclidine molecule. The description of the methods of synthesis of various quinuclidine derivatives features prominently in the review. These data are presented with separate discussion of the methods of synthesising the bicyclic quinuclidine system and the methods for the introduction of various substituents into the preformed quinuclidine ring. This system made it possible to give a general account of the abundant factual data which have accumulated so far on the synthesis of quinuclidine derivatives and to emphasise the characteristics of the synthetic studies on this class of substances.
A special section deals with the comparatively new reactions involving the expansion of the quinuclidine ring. The bibliography comprises 227 references.

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I. INTRODUCTION

The heterocyclic quinuclidine 1-azabicyclo[2,2,2]octane system is a structural fragment in a number of natural physiologically active substances and synthetic medicinal preparations†.

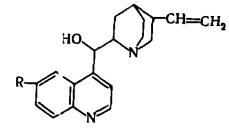
Among natural alkaloids, derivatives of quinoline and indole, containing the quinuclidine ring in the molecule, mention should be made of the cinchonine–cinchonamine (alkaloids of the bark of the cinchona tree)[8–12], sarpagine–ajmaline (Rauwolfia alkaloids)[8,13,14], and macusaine (strychnine alkaloids)[15,16] groups.

In connection with the high chemotherapeutic activity of the cinchona alkaloids, among which quinine occupies a particularly important place as an antimalarial drug, the study of the methods of synthesis of quinine and its analogues has occupied the attention of investigators in many countries for a long time. The ability of natural quinuclidine compounds (quinidine, ajmaline) to reduce the capacity of heart muscle to be stimulated, the comparatively recently discovered high pharmacological activity of certain synthetic quinuclidine derivatives and its wide variety, and the possibility of employing quinuclidine compounds as catalysts for the synthesis of polymers[17] have all stimulated further interest in studies on the quinuclidine series.

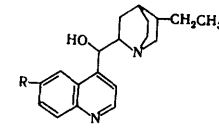
Among important advances in the investigation of natural quinuclidine compounds, mention should be made of the total synthesis of quinine achieved by Woodward and Doering[18] in 1944 and also the synthesis of cinchonamine carried out in 1958 by Ch'ên Ch'ang-Pai et al.[19] The total synthesis of racemic homomeroquinene, an intermediate in the synthesis of quinine, was achieved by Rubtsov from trichlorocollidine[20].

† Previously a number of reviews were published giving a fairly complete description of the development of the chemistry of quinuclidine derivatives[1–7].

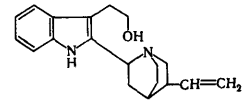
Alkaloids of the cinchonine–cinchonamine group



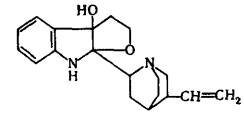
R = H cinchonine, cinchonidine
R = OH cupreine
R = OCH_3 quinine, quinidine, epiquinine, epiquinidine



R = H hydrocinchonine, hydrocinchonidine
R = OCH_3 hydroquinidine, hydroquinine

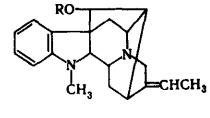


cinchonamine

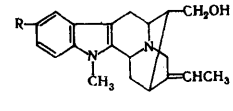


quinamine, conquinamine

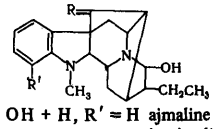
Alkaloids of the sarpagine, ajmaline, and macusaine group



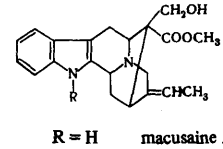
R = H tetraphyllicine
R = $(CH_3O)_3C_6H_2CO$ rauvomitine



R = OH sarpagine
R = OCH_3 lochnerine



R = OH + H, R′ = H ajmaline, isoajmaline, sandwicine
R = O, R′ = H ajmalidine
R = O, R′ = OCH_3 vamalidine



R = H macusaine A
R = CH_3 voachalotine

A number of reviews have been devoted[8-12,21], to problems connected with the chemistry of natural quinuclidine compounds and in particular the history of their discovery and practical applications, the examination of the natural sources, the methods of analysis and isolation, the determination of the structure and reactions of these compounds, and also problems of their stereochemistry. Therefore these data need not be described again and attention may be concentrated in the present review on the general chemical characteristics of quinuclidine derivatives, the methods of synthesising the quinuclidine ring and introducing substituents into the quinuclidine molecule, and also the biological properties of synthetic quinuclidine derivatives.

II. SOME CHARACTERISTICS OF QUINUCLIDINE DERIVATIVES

Quinuclidine (I) is the saturated bicyclic system with a nodal nitrogen atom

(I)

In contrast to aliphatic tertiary amines and *N*-substituted piperidines, quinuclidine has a rigidly fixed structure. The atoms comprising the quinuclidine ring are incapable of altering their relative positions by rotating about their bonds, which are included in a bicyclic system where each ring has the "boat" form. Compared with other 1-azabicycloalkanes, quinuclidine is characterised by high symmetry and only slight strain of the cyclic system. A distinctive feature of the quinuclidine molecule is also almost complete absence of screening of the sp^3-hybridised unshared electron pair at the nitrogen atom. These characteristics of the structure explain many physical and chemical properties of both quinuclidine itself and its various derivatives. For example, quinuclidine is a volatile crystalline substance with a high melting point (158°C). It readily sublimes even on standing in air. Breakdown of the symmetry of the quinuclidine molecule (by its conversion into condensed systems or by introduction of alkyl substituents) leads to a lowering of the melting point[22-26].

Interesting results were obtained in a comparative study of the infrared spectra of quinuclidine and piperidine and piperazine derivatives substituted at the nitrogen atom[27]. The spectra of the monocyclic compounds show in the range 2700–2800 cm^{-1} characteristic absorption bands due to the interaction of the free electron pair of the nitrogen atom with the adjacent axial C–H bonds. Quinuclidine does not absorb in this region, probably because of the absence of such interaction. Characteristic absorption bands at 2430, 2915, and 3405 cm^{-1} have been noted for quinuclidine[28].

The basicity of quinuclidine, which depends on the electron density at the nitrogen atom, is fairly high and close to that of the lower aliphatic amines and *N*-alkylpiperidines. The basicity of the condensed systems of benzo- and dibenzo-quinuclidine is reduced because of the inductive effect of the phenyl groups[26,29]. Comparison of the pK_a of the benzo- and dibenzo-quinuclidines with those of diethylaniline and diphenylamine, which have similar structures, demonstrates clearly the effect of the rigidity of the structure of quinuclidine derivatives (Table)[30].

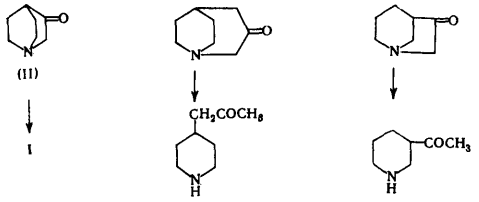
Like other aliphatic tertiary amines, quinuclidine readily forms salts with mineral and organic acids and also quaternary derivatives with alkyl halides. However, kinetic studies have shown[32] that the rate of reaction of alkyl iodides with quinuclidine is much higher than in similar reactions with aliphatic tertiary amines. For example, quinuclidine reacts with methyl iodide 50 times faster and with isopropyl iodide 700 times faster than does triethylamine. The trimethylborane adduct of quinuclidine proved to be more stable than the corresponding adducts of the trialkylamine series. These results can be explained by the virtual absence of steric hindrance at the electron pair of the nitrogen of the bicyclic system.

pK_a values for quinuclidine and related compounds

Compound	pK_a	References
Dimethylamine	10.77	31
Diethylamine	10.93	31
Triethylamine	10.87	31
N-Methylpiperidine	10.08	31
Quinuclidine	10.58	26
Benzoquinuclidine	7.79	26
Diethylaniline	6.56	31
Dibenzoquinuclidine	4.46	26
Diphenylamine	0.79	31.

The considerable chemical stability of the quinuclidine molecule is associated with the characteristics of its structure. Quinuclidine does not change on heating with concentrated mineral acids and on oxidation with potassium permanganate[22].

Leonard et al.[33] showed that, when 3-quinuclidone (II) is subjected to the Clemmensen reduction, the quinuclidine ring is retained, while ring fission occurs in other 1-azabicyclic ketones:

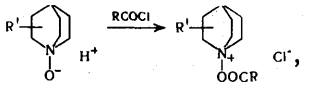


Quinuclidine is not dehydrogenated by mercury acetate, probably because in this case the reaction would have to proceed via a salt of Δ^1-dehydroquinuclidine and the formation of the latter is impossible according to the Bredt rule[2,34]. Quinuclidine can be dehydrogenated only under severe conditions (300°C) using palladium on charcoal or selenium[35]. The C–N bond then breaks and 4-ethylpyridine is formed.

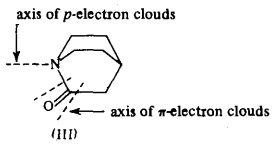
The pyrolysis and hydrogenolysis of quaternary quinuclidine salts leads to high yields of quinuclidine[2,36-38]. The formation of tertiary amines, in this case due to the elimination of aliphatic alcohols, is also a fundamental process accompanying the Hofmann degradation of quaternary quinuclidinium bases[39-41]. For example, in the Hofmann degradation of 1-methylquinuclidinium hydroxide unsubstituted quinuclidine was isolated in 35% yield together with products obtained as a result of the opening of the quinuclidine ring—1-methyl-4-vinylpiperidine and 1-methyl-4-(β-hydroxyethyl)piperidine[39]. All these findings constitute additional confirmation of the thermal and chemical stability of the quinuclidine ring.

The *N*-oxides of quinuclidine derivatives are capable of forming *O*-acylium salts which are stable to hydrolysis in neutral or acid media. On the other hand, their sensitivity

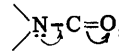
to alkalis is so high that they can be titrated as dibasic acids[42]:

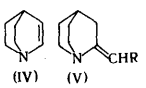


where R = CH_3 or C_6H_5. Interesting chemical properties have been found in bicyclic amides of the type of 2-quinuclidone (III).[43-46] The axes of the free *p*-electron clouds of nitrogen in such compounds prove to be almost perpendicular to the axes of the π-electron clouds of the carbonyl group:

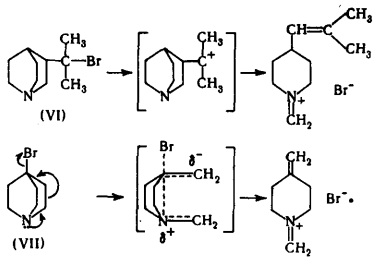


(III)

As a result, conjugation of the type  , which is characteristic of amides, is impossible in 2-quinuclidones. A number of properties of 2-quinuclidones, which makes them similar to amino-ketones, are connected with this fact. The nitrogen atom in 2-quinuclidones is readily protonated (ordinary amides and lactams are protonated at the oxygen) and methylated; 2-quinuclidones are highly basic (pK_a = 5.33–5.6)[44] compared with other amides (for example, *N*-acetylpiperidine has pK_a = 0.4). In the infrared spectra of these substances the frequency of the C=O stretching vibrations is on the average higher by 80 cm^{-1} than in ordinary lactams and the integral intensity of the carbonyl band is smaller by a factor of almost 2. The absorption maxima of 2-quinuclidones in the ultraviolet spectra occupy a position intermediate between the maxima of amides and ketones. The absence of amide mesomerism in 2-quinuclidones results in an increase of their reactivity, which is reflected in a higher rate of hydrolysis and alcoholysis of their hydrochlorides. The kinetics of the above reactions can be investigated by polarography, while normal amides and lactams cannot be reduced polarographically. The high reactivity of the C=O group in 2-quinuclidones is reflected also in the acidity of the adjacent CH_2 groups, which shows a tendency to undergo deuterium exchange. Finally, the C=O group in 2-quinuclidone is capable of nucleophilic substitution reactions which are characteristics of ketonic carbonyls—for example the formation of oximes with hydroxylamines[43]. Certain unusual chemical features are shown also by unsaturated quinuclidine derivatives—Δ^2-dehydroquinuclidine (IV),[47,48] its 2-substituted derivatives[49], and quinuclidines (V) with an exocyclic double bond in the 2-position[49]. As was to be expected on the grounds of structural considerations, these compounds differ in their properties from normal tertiary α-vinylamines. For example, dehydroquinuclidines do not exhibit the absorption at 230 nm characteristic of enamines and are not hydrolysed under mild conditions by dilute acids.


(IV) (V)

In contrast to the analogous aliphatic and nitrogen-free bicyclic compounds, the fragmentation of quinuclidine derivatives[50-57] takes place unambiguously. 2-(Quinuclidin-3′-yl)-2-bromopropane (VI) undergoes solvolysis by a stepwise mechanism[50,51] and 4-bromoquinuclidine (VII) is solvolysed by a synchronous mechanism[50,53]:


(VI)

(VII)

Because of the ease of protonation of the nitrogen atom in the quinuclidine ring, the competing reactions involving the isomerisation of the carbonium ion and also substitution and elimination processes do not play a significant role in these cases.

III. METHODS OF SYNTHESIS OF QUINUCLIDINE AND ITS DERIVATIVES

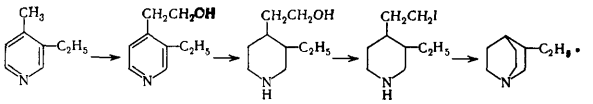
In the course of investigations over a period of many years a large number of a wide variety of quinuclidine derivatives have been synthesised. In order to give a systematic account of the literature data and the methods of preparation of quinuclidine and its substituted derivatives, in this review a distinction is drawn between methods of synthesis associated with the formation of the quinuclidine ring and methods for the introduction of various substituents into the preformed quinuclidine ring. Reactions accompanied by the expansion of the quinuclidine ring with formation of derivatives of other 1-azabicycloalkanes are described in a special section.

1. METHODS FOR QUINUCLIDINE RING CLOSURE

The starting compounds for the formation of the quinuclidine ring may be both piperidine derivatives and aliphatic substances: trihalogenoalkanes and dihalogenoalkylamines. The piperidine derivatives are obtained mainly from pyridine bases. Dihalogenoalkylamines and trihalogenoalkanes are usually synthesised from tetrahydropyran derivatives, dialkoxymalonic esters, or alkanetricarboxylic acid esters.

The quinuclidine ring closure is as a rule achieved by two mechanisms when piperidine derivatives are used: (1) by intramolecular alkylation or acylation or (2) by Dieckmann's intramolecular cyclisation.

Intramolecular alkylation was proposed in 1904 by Koenigs[58,59] for the preparation of the first synthetic representative of the quinuclidine series—3-ethylquinuclidine (VIII):


(IX) (X) (XI) (VIII)

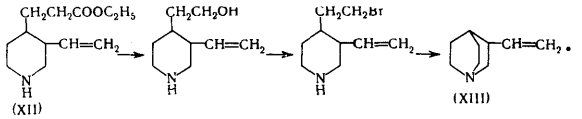
The starting material in Koenigs scheme was 3-ethyl-4-methylpyridine (IX). The product of the condensation of compound (IX) with formaldehyde was reduced with sodium in alcohol. The hydroxy-group in the piperidine derivative (X) obtained was replaced by iodine and 3-ethyl-4-(β-iodoethyl)piperidine (XI) was cyclised under the influence

of sodium carbonate with formation of 3-ethylquinuclidine (VIII).

A similar scheme using 4-methylpyridine as the starting material was employed in 1909 by Löffler and Stitzel[60] to prepare unsubstituted quinuclidine. However, these workers were unable to isolate pure quinuclidine and it was not until 1920 that Meisenheimer[22] obtained it. Meisenheimer[22] also described the conversion of 4-methylquinoline into benzoquinuclidine by Koenigs' method.

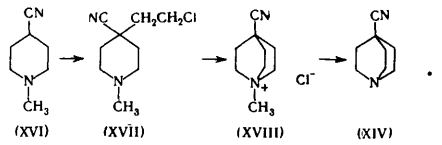
Later intramolecular alkylation of 4-(β-halogenoalkyl)-piperidines in the presence of alkaline reagents (sodium hydroxide, sodium bicarbonate, potassium carbonate, pyridine, etc.) was used frequently to synthesise quinuclidine[61] and its various derivatives. 2-Methylquinuclidine[23,62,63], 4-methylquinuclidine[25], dibenzoquinuclidine[26], 3-hydroxymethyl-3-methylquinuclidine[36,37,64], the lactone of 3-carboxymethyl-3-hydroxymethylquinuclidine[65], etc. were obtained by this procedure.

Lukeš and Galik[66] converted by a similar procedure the ethyl ester of meroquinene (XII), isolated from natural cinchonine, into optically active 3-vinylquinuclidine (XIII):



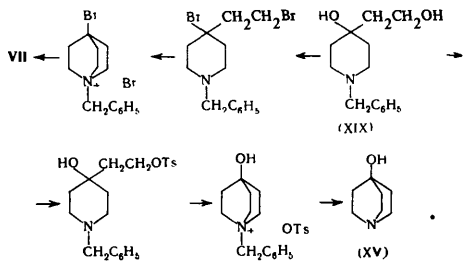
(XII) (XIII)

Grob et al.[67,68] used Koenigs' method to prepare 4-monosubstituted quinuclidines, including 4-cyano- (XIV), 4-bromo- (VII), and 4-hydroxy-quinuclidines (XV). The cyclisation in these syntheses was not based on secondary amines of the piperidine series but was carried out using tertiary *N*-substituted (*N*-methyl- and *N*-benzyl-)piperidines:



(XVI) (XVII) (XVIII) (XIV)

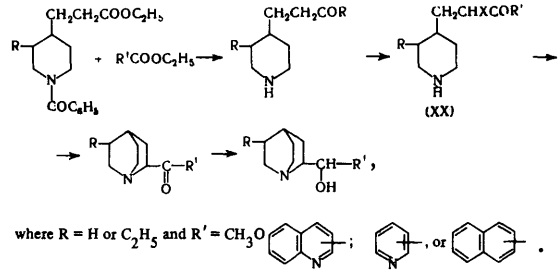
For example, 4-(β-chloroethyl)-4-cyano-1-methylpiperidine (XVII), obtained by the condensation of 4-cyano-1-methylpiperidine (XIV) with dichloroethane, was cyclised to the methochloride of 4-cyanoquinuclidine (XVIII), from which methyl chloride was eliminated on heating in a vacuum to 260–270°C.[67] The analogous conversion of 1-benzyl-4-hydroxy-4-(β-hydroxyethyl)piperidine (XIX) into 4-bromoquinuclidine (VII) and 4-hydroxyquinuclidine (XV)[68] can be represented as follows:



(XIX) (XV)

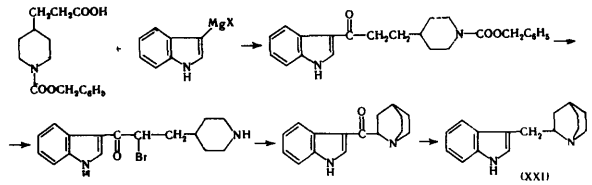
Rabe[69,70] and later other investigators[71–75] employed the above method of formation of the quinuclidine ring in their syntheses of analogues and isomers of cinchona alkaloids.

In this case the starting materials were not 4-halogenoalkyl piperidines or the analogous tosyl esters but halogeno-oxo-derivatives of the piperidine series—4-(β-halogeno-γ-oxoalkyl)piperidines (XX), the syntheses and reactions of which are shown below:



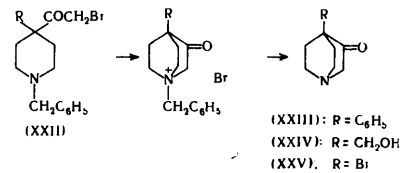
(XX)

A similar scheme was employed also in the synthesis of 2-scatylquinuclidine (XXI):[76]



(XXI)

Starting with the halogeno-oxo-derivatives of piperidine of another type, compounds of the 4-(β-bromo-α-oxoethyl)-piperidine (XXII) series, 3,4-disubstituted quinuclidines were prepared: 3-oxo-4-phenylquinuclidine (XXIII),[38] 4-hydroxymethyl-3-oxoquinuclidine (XXIV),[77] and 4-bromo-3-oxoquinuclidine (XXV):[78]

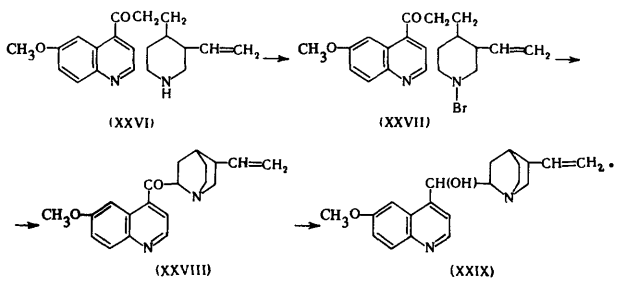


(XXII)

(XXIII): R = C_6H_5
(XXIV): R = CH_2OH
(XXV): R = Br

It was then shown[78] that quinuclidine ring closure is possible only with the axial disposition of both the 4-bromoacetyl residue and of the electron pair at the nitrogen atom. The formation of this conformation in the transition state is facilitated by the introduction of bulky substituents in the 1- and 4-positions of the piperidine ring. The attempts to cyclise compounds without such substituents (for example, 4-bromoacetylpiperidine) were unsuccessful[78].

Rabe[79,80] developed a somewhat different method of quinuclidine ring closure for the synthesis of cinchona alkaloids containing the vinyl group in the molecule. In this case it is difficult to introduce a halogen into the oxoalkyl residue of 4-oxoalkyl-3-vinylpiperidines (XXVI) without affecting the double bond. Therefore *N*-bromo-substituted and not *C*-substituted piperidines were employed for quinuclidine ring closure:

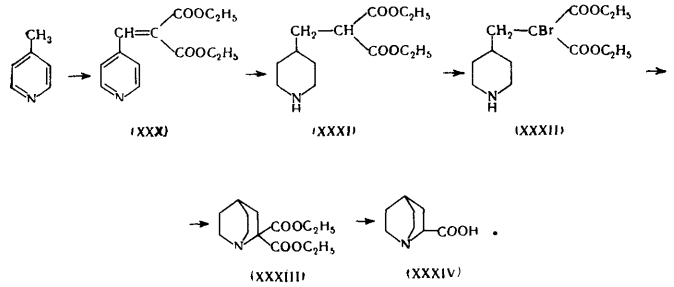


(XXVI) (XXVII) (XXVIII) (XXIX)

Quinotoxine (XXVI) was converted by treatment with sodium hypobromite into *N*-bromoquinotoxine (XXVII), which was cyclised under the influence of alkoxides to the corresponding quinuclidine derivative—quininone (XXVIII). The scheme developed by Rabe was used in the total synthesis of quinine (XXIX)[18] and also for the preparation of a number of analogues of this alkaloid[81,82].

In contrast to the unambiguous cyclisation of *N*-halogeno-4-oxoalkylpiperidines, considerable difficulties were encountered when 4-alkyl-*N*-halogenopiperidines were used for quinuclidine ring closure. Wawžonek and coworkers[83,84,87] and Lukeš and coworkers[85,86,88] established that the application of the Hofmann–Löffler reaction to 4-alkyl-*N*-chloropiperidines leads to the formation of a mixture of products in which quinuclidine derivatives are present together with the isomeric alkyl-1-azabicyclo[2,2,1]heptanes. The treatment of *N*-(β-chloroethyl)piperidine or its derivatives with a methanol solution of potassium hydroxide[27,89] leads to the formation of Hofmann degradation products, arising in the synthesis of 1,4-bispentamethylenepiperazinium dichloride. The main product is 1,2-bis(*N*-piperidino)ethane[27].

The Koenigs reaction was developed further in the work of Rubtsov, Dorokhova, and Mikhlina[90,91] and also Grob and coworkers[92,93], who employed α-halogeno-acids of the piperidine series and their esters for intramolecular alkylation. Rubtsov and Dorokhova[90] developed in 1953 a simple method for the synthesis of quinuclidine-2-carboxylic acid in five stages:

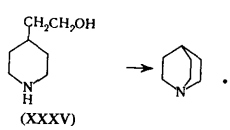


(XXX) (XXXI) (XXXII) (XXXIII) (XXXIV)

The condensation of γ-picoline with mesoxalic ester gave 4-(ββ-diethoxycarbonylvinyl)pyridine (XXX). The unsaturated ester (XXX) was hydrogenated using platinum to compound (XXXI), which was then treated with bromine. The resulting 4-(β-bromo-ββ-diethoxycarbonylethyl)piperidine (XXXII) was cyclised in the presence of pyridine to 2,2-diethoxycarbonylquinuclidine (XXXIII). The latter was hydrolysed and partially decarboxylated with formation of quinuclidine-2-carboxylic acid (XXXIV).

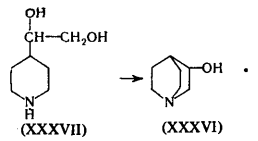
The above principle involving the cyclisation of α-halogeno-esters of the piperidine series was widely employed subsequently for the synthesis of various 2,3- and 2,5-disubstituted quinuclidines: 3-carboxymethylquinuclidine-2-carboxylic acid[94], 3-methylquinuclidine-2-carboxylic acid[95], and 5-[β-hydroxy(methoxy)ethyl]quinuclidine-2-carboxylic acid[96,97].

A variant of the intramolecular alkylation method is the gas-phase cyclodehydration of 4-(β-hydroxyethyl)piperidine (XXXV) proposed by Leonard et al.[98]:



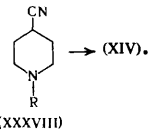
(XXXV)

The same method was used to synthesise 3-hydroxyquinuclidine (XXXVI) from piperid-4'-ylethane-1,2-diol (XXXVII):[99]



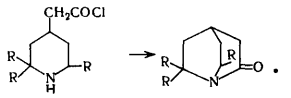
(XXXVII) (XXXVI)

Another variant of the intramolecular alkylation method is the synthesis of 4-cyanoquinuclidine (XIV) by the condensation of 1-alkyl-4-cyanopiperidines (XXXVIII) with ethylene glycol esters in the presence of alkali metals[100]:

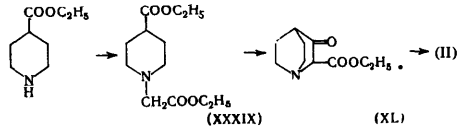


(XXXVIII)

The intramolecular acylation of piperidine derivatives has been used together with intramolecular alkylation for the formation of the quinuclidine ring. Yakhontov and Rubtsov and subsequently Pracejus and coworkers synthesised in this way 2-quinuclidone (III)[43] and its 6,6-dimethyl-[44] and 6,6,6-trimethyl-[45,101] derivatives from the corresponding acid chlorides under the influence of anhydrous potassium carbonate or tertiary amines:



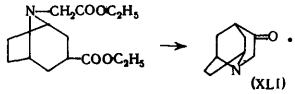
Another method for the closure of the quinuclidine ring is based on Dieckmann's *intramolecular cyclisation*. This procedure was proposed for the first time by Clemo and Metcalfe[102] for the synthesis of 3-quinuclidone (II):[102]



(XXXIX) (XL)

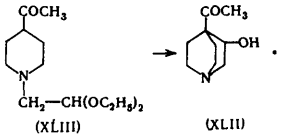
Ethyl isonipecotate was converted by alkylation with chloroacetic ester into ethyl 1-ethoxycarbonylmethylisonipecotate (XXXIX). The latter was cyclised in the presence of metallic potassium in toluene and the resulting β-keto-ester (XL) was hydrolysed and decarboxylated without isolation. Later this method was improved and the yield of the ketone (II) in the cyclisation stage was increased to 84%.[103-107]

The isolation of the intermediate in the synthesis—ethyl 3-oxoquinuclidine-2-carboxylate (XL)[108]—made it possible to develop methods based on it for the preparation of various 2,3-disubstituted quinuclidines[49,108,109]. Subsequently the Clemo reaction was used to synthesise ring-substituted quinuclidines: 5-oxoquinuclidine-2-carboxylic acid[110], 6-methyl-3-quinuclidone[111], 6,7-dimethyl-3-quinuclidone[112], and also compounds of the tropaquinuclidine series (XLI):[113]



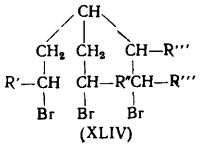
(XLI)

The recently described quinuclidine ring closure by intramolecular aldol condensation in the synthesis of 4-acetylquinuclidin-3-ol (XLII) from 4-acetyl-1-(2′,2′-diethoxyethyl)piperidine (XLIII) [77] is unusual:



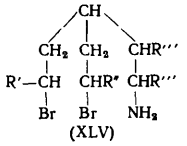
(XLIII) (XLII)

A fundamentally different approach to the synthesis of quinuclidine and its derivatives was developed by Prelog and coworkers [114,115]. The methods which they proposed are based on the action of ammonia under pressure at 100–120°C on tribromoalkanes (XLIV):



(XLIV)

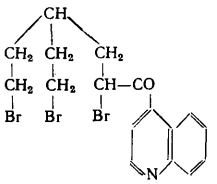
or on double intramolecular alkylation consisting in the treatment with alkali of dibromoalkylamines (XLI):



(XLV)

Quinuclidine [39,114-117], its 2-alkyl- [23,24], 3-alkyl- [24], and 4-alkyl-derivatives [25], and also quinuclidine-2-carboxylic acid [118] were obtained in this way.

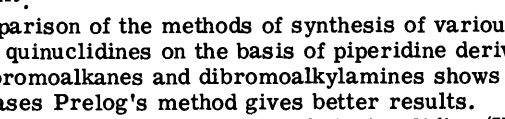
Prelog's attempts to achieve the cyclisation of the tribromoalkyl derivative (XLVI),



(XLVI)

in order to obtain a quinine analogue proved to be unsuccessful [119].

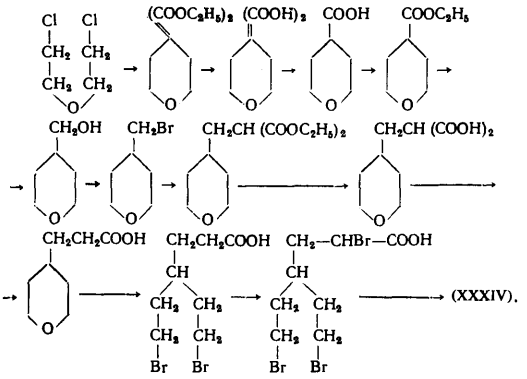
Comparison of the methods of synthesis of various substituted quinuclidines on the basis of piperidine derivatives and tribromoalkanes and dibromoalkylamines shows that in some cases Prelog's method gives better results. For example, in the synthesis of 2-methylquinuclidine (XLVII) by this procedure Lukeš achieved a yield of 37%: [23]



(XLVII) (XLVIII)

The sole example of 3,5-disubstituted quinuclidines described, 3,5-dimethylquinuclidine (XLVIII), [120] was synthesised by Prelog's method.

At the same time the synthesis of quinuclidine derivatives from tribromoalkanes and dibromoalkylamines involves in many cases starting materials which are difficult to obtain and are formed in multistage syntheses with low yields. Prelog's method is also less suitable for the synthesis of quinuclidine derivatives containing functional groups. As an example, one may quote the methods of preparation of quinuclidine-2-carboxylic acid (XXXIV): [118]



In this case the synthesis of compound (XXXIV) is achieved by a multistage procedure (12 stages) and the overall yield is about 4%. In the five-stage synthesis of compound (XXXIV) starting with γ-picoline described above the yield of quinuclidine-2-carboxylic acid is 30%. [90]

2. METHODS FOR THE INTRODUCTION OF SUBSTITUENTS INTO THE QUINUCLIDINE RING

As already mentioned above, the quinuclidine molecule is a saturated bicyclic system. The introduction into this molecule of functional groups by direct substitution presents considerable difficulties and experiments of this kind have not been carried out at all so far. Therefore reactive groups are usually introduced during the closure of the quinuclidine ring and are then used to convert the product into various classes of quinuclidine derivatives. The most readily available compounds containing such functional groups are the carboxy- and carbonyl derivatives: quinuclidine-2-carboxylic acid, 3-quinuclidone, and others. Almost all substituted quinuclidine derivatives of a wide variety of types were obtained from the carboxy- and carbonyl derivatives using the usual methods of organic synthesis.

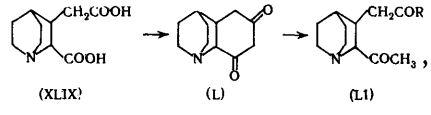
(1) Syntheses of Substituted Quinuclidines from Quinuclidinecarboxylic Acids

At the present time all three monocarboxylic acids of quinuclidine are known: quinuclidine-2-carboxylic [90,118], quinuclidine-3-carboxylic [121,122], and quinuclidine-4-carboxylic [67,100], and also quinuclidine-2-carboxylic acids with various substituents in the 3-position [95,108] and the 5-position [96,110] and quinuclidine-3-carboxylic acids with substituents in the 2-position [123] and the 6-position [111]. Only one compound containing 2-carboxy-groups in the quinuclidine ring has been described: quinuclidine-2,3-dicarboxylic acid [109]. A large number of homologues of quinuclidinecarboxylic acids have been obtained, among which quinuclidine-3-acetic [124-127] and 3-carboxymethylquinuclidine-2-carboxylic acid [94] are of definite interest for further reactions. The syntheses of quinuclidine derivatives from quinuclidinecarboxylic acids may be divided into three large groups: (a) reactions without change in the length of the carbon chain; (b) reactions accompanied by the dissociation of the C–C bond and a decrease in chain length;

(c) reactions associated with an increase in the length of the carbon chain.

a. Reactions without change in the length of the carbon chain. Quinuclidinecarboxylic acids readily form acid chlorides which can be converted without isolation into the corresponding esters [67,96,125,128-130] or amides [125,130,131]. It is noteworthy that other methods have also been used to prepare the esters of quinuclidinecarboxylic acids; esterification in the presence of sulphuric acid and hydrogen chloride and also transesterification with alkali metal alkoxides [96,109,110]. The amides of Δ^2-dehydroquinuclidine-2- and -3-carboxylic acids were obtained from the corresponding esters by the action of alcoholic ammonia [47,49]. Esters of quinuclidinecarboxylic acids have also been used to synthesise many hydrazides and their hydrazones [95,132] and the amides were used to synthesise nitriles [47,49,90].

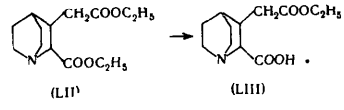
The attempt to obtain the anhydride from 3-carboxymethylquinuclidine-2-carboxylic acid (XLIX) in the presence of acetic anhydride and sodium acetate unexpectedly led to the formation of the tricyclic β-diketone (L). [133] On interaction with substances with a mobile hydrogen atom (water, alcohols, amines), the latter readily underwent ring opening with formation of derivatives of 2-acetylquinuclidine-3-acetic acid (LI): [133]



(XLIX) (L) (LI)

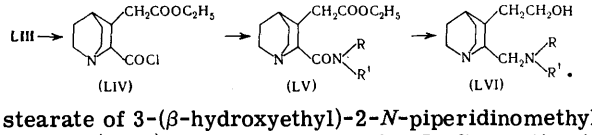
where R = OH, OC_2H_5, or NR'_2.

Esters of acids of the quinuclidine series are readily hydrolysed, the reaction being particularly easy for alkoxycarbonyl groups in the α-position of the quinuclidine ring [134]. On prolonged storage of aqueous solutions of diethyl 3-carboxymethylquinuclidine-2-carboxylate (LII) at room temperature, the acid ester (LIII) is formed [134], and this has been used to synthesise compounds containing various functional groups in the 2- and 3-positions of the quinuclidine ring:



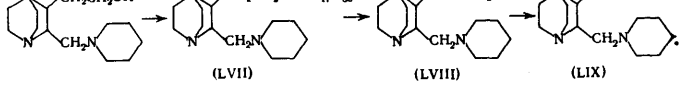
(LII) (LIII)

For example, when compound (LIII) reacts with thionyl chloride, the monochloride (LIV) forms readily and in the presence of primary and secondary amines is converted into the amides of 3-ethoxycarbonylmethylquinuclidine-2-carboxylic acid (LV). [130,134] The reduction of these amidoesters with lithium aluminium hydride leads to 2-alkyl(dialkyl)-3-(β-hydroxyethyl)aminomethylquinuclidines (LVI):



(LIV) (LV) (LVI)

The stearate of 3-(β-hydroxyethyl)-2-*N*-piperidinomethylquinuclidine (LVII) was converted by the Kraft reaction into the unsaturated compound (LVIII) from which 2-*N*-piperidinomethylquinuclidine-3-carboxylic acid (LIX) was obtained by oxidation with potassium permanganate [123]:

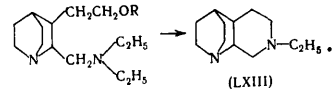


(LVII) (LVIII) (LIX)

The formation as a result of the above reactions of a derivative of quinuclidine-3-carboxylic acid (LIX) is convincing proof that the ethoxycarbonyl group in the 2-position is the first to be hydrolysed in the diethyl ester (LII).

A similar phenomenon obtains also in the diethyl ester of quinuclidine-2,3-dicarboxylic acid [109], which is consistent with the known greater ease of hydrolysis of α-amino-acid esters compared with β-amino-acid esters.

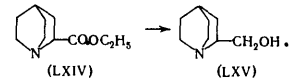
The unusual reaction of 2-diethylaminomethyl-3-(β-hydroxyethyl)quinuclidine is noteworthy [123]. It has been found that, on distillation under atmospheric pressure, compounds (LX) and (LXI) cyclise with elimination of an ester molecule and the formation of a new tricyclic system—*N*-ethylpiperidino[3,4-*b*]quinuclidine (LXIII). The corresponding amino-alcohol (LXII) behaves analogously on heating with phthalic anhydride in the presence of benzenesulphonic acid [123]:



(LXIII)

(LX): R = COC_6H_5
(LXI): R = $COC_{17}H_{35}$
(LXII): R = H

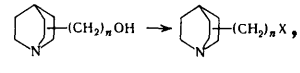
The reduction of ethyl quinuclidine-2-carboxylate (LXIV) by the Bouveault–Blanc method or with lithium aluminium hydride yields quinuclidin-2-yl-methanol (LXV): [24]



(LXIV) (LXV)

The second reduction procedure is easier to handle and gives better yields and therefore lithium aluminium hydride is mainly used in most studies for the preparation of various alcohols [67,95,121,125,134] and glycols [94,109] of the quinuclidine series.

Halogenoalkylquinuclidines have been synthesised by the reaction of the corresponding alcohols with thionyl chloride or hydrogen halides [24,49,121,135,136]:



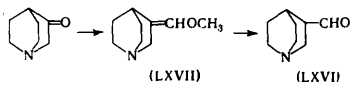
where $n = 1$ or 2.

Examination of the chemical properties of halogenoalkyl-substituted quinuclidines shows that the halogen atoms in the 2-halogenomethyl group are not very labile: for example, 2-chloromethylquinuclidine does not react with ammonia and amines [137] and the corresponding reactions of 2-bromomethylquinuclidine take place with low yields [137].

Although the halogen atoms in 3-halogenoalkylquinuclidines are more reactive, the use of compounds of this type as starting materials in various syntheses is made difficult by the ease of their conversion into quaternary polymeric derivatives [136]. These features of halogeno-derivatives of quinuclidine limit their application only to those cases where powerful nucleophilic agents are employed. Therefore the principal method for the synthesis of aminoalkylquinuclidines is not the interaction of halogeno-derivatives of quinuclidines with amines but the reduction with lithium aluminium hydride of the corresponding quinuclidinecarboxylic acid amides [122,130,131,138].

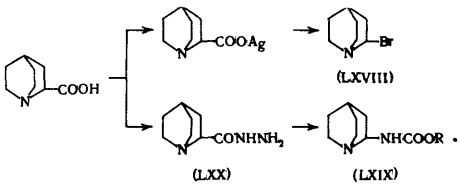
Aldehydes of the quinuclidine series are of considerable interest for the synthesis of various quinuclidine derivatives. At the present time all three monoformylquinuclidines are known. 2-Formylquinuclidine and 3-formylquinuclidine [139,140] have been obtained by the reduction of the

N-methylanilides of the corresponding quinuclidinecarboxylic acid with a calculated amount of lithium aluminium hydride or by the reduction of the ethyl esters of these acids with sodium aluminium hydride; 4-formylquinuclidine[67] has been obtained by the oxidation of quinuclidin-4-ylmethanol with potassium dichromate. 3-Formylquinuclidine (LXVI) has also been synthesised from 3-quinuclidone by its reaction with methoxymethylenetriphenylphosphorane and subsequent hydrolysis of 3-methoxymethylenequinuclidine (LXVII) with hydrochloric acid[141]:



(LXVII) (LXVI)

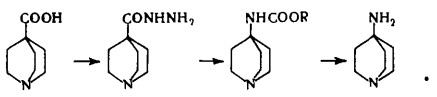
b. Reactions accompanied by the dissociation of a C—C bond and a decrease in the length of the carbon chain. Substances with less carbon atoms have been synthesised from quinuclidine-2-carboxylic acid: 2-bromoquinuclidine (LXVIII)[90] and urethanes of 2-aminoquinuclidine (LXIX).[142] These compounds are of considerable interest, since they contain at the same carbon atom a bromine atom and an amino-group (in 2-bromoquinuclidine) or two amino-residues (in 2-aminoquinuclidine derivatives). Such combination of functional groups leads to the appearance of new chemical properties in these compounds. For example, compound (LXVIII) does not form Grignard reagents and compound (LXIX) is so stable that in the hydrolysis of its urethanes under mild conditions ammonia is eliminated and polymers of dehydroquinuclidine are formed. The synthesis of compound (LXVIII) was achieved using the Borodin reaction[90]; the urethanes of compound (LXIX) were obtained starting with the hydrazide of quinuclidine-2-carboxylic acid (LXX) by the Curtius reaction[142]:



(LXVIII)

(LXX) (LXIX)

Analogous reactions in the quinuclidine-4-carboxylic acid series made it possible to obtain 4-aminoquinuclidine (LXXI):[143]

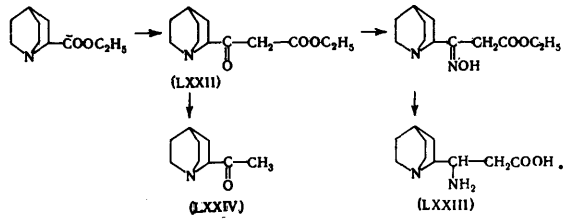


(LXXI)

The same compound was synthesised directly from quinuclidine-4-carboxylic acid by the Schmidt reaction. However, despite the greater number of stages, the first method proved to be more rational.

c. Processes associated with the growth of the carbon chain. Claisen, Grignard, etc. reactions have been used to synthesise quinuclidine derivatives with increase in the length of the carbon chain.

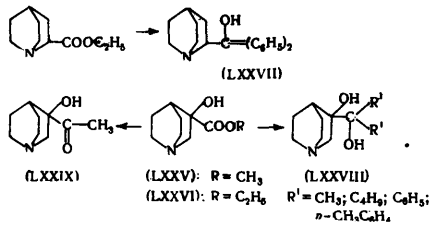
The Claisen condensation of ethyl quinuclidine-2-carboxylate with ethyl acetate led to the formation of ethyl β-oxo-β-(quinuclidin-2-yl)propionate (LXXII), which was then further converted into β-amino-β-(quinuclidin-2-yl)-propionic acid (LXXIII)[108] and 2-acetylquinuclidine (LXXIV):[43]



(LXXII)

(LXXIV) (LXXIII)

The carbinols (LXXVII)[24] and pinacones (LXXVIII)[144] were obtained by the Grignard reaction from the esters of quinuclidine-2-carboxylic and 3-hydroxyquinuclidine-3-carboxylic acids [compounds (LXXV) and (LXXVI)] respectively:

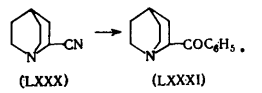


(LXXVII)

(LXXIX) (LXXV): R = CH_3 (LXXVIII)

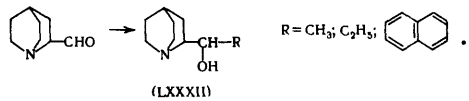
(LXXVI): R = C_2H_5 R' = CH_3; C_4H_9; C_6H_5; *n*-$CH_3C_6H_4$.

It is noteworthy that in the interaction of the hydroxy-ester (LXXV) with methylmagnesium iodide the process terminates at the stage involving the formation of the ketone (LXXIX). A Grignard reaction has also been described for 2-cyanoquinuclidine (LXXX), which was converted into 2-benzoylquinuclidine (LXXXI):[49]



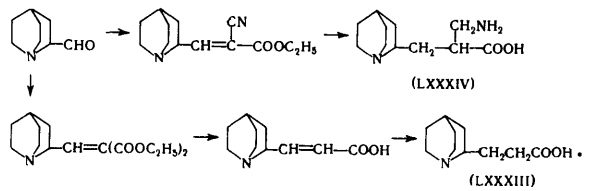
(LXXX) (LXXXI)

The introduction of 2-formylquinuclidine into reactions with organomagnesium compounds led to the development of a new method of synthesis of quinuclidin-2-ylmethanols (LXXXII) which are analogues of cinchona alkaloids[145]:



(LXXXII)

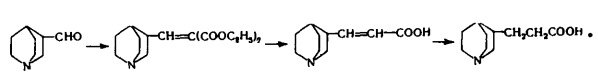
The condensation of 2-formylquinuclidine by the Knoevenagel reaction with cyanoacetic[108] and malonic[129] esters was used to synthesise quinuclidine-2-β-propionic acid (LXXXIII) and its α-aminomethyl derivative (LXXXIV):



(LXXXIV)

(LXXXIII)

Quinuclidine-3-β-acrylic and quinuclidine-3-β-propionic acids were synthesised similarly from 3-formylquinuclidine[140]:

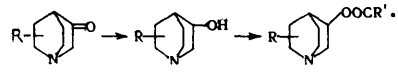


The malonic ester synthesis was used to prepare quinuclidine-2-β-propionic acid from 2-bromomethylquinuclidine[128] and quinuclidine-3-γ-butyric acid from 3-(β-chloroethyl)quinuclidine[125].

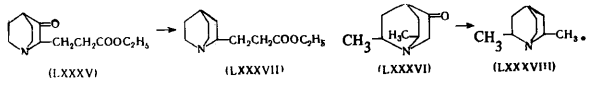
(2) Syntheses of Substituted Quinuclidines from 3-Quinuclidone

Among oxo-derivatives of quinuclidine the most readily available is 3-quinuclidone. The derivatives of 2-quinuclidone have been little investigated and at the present time are hardly used as starting materials in synthetic studies. There is an extremely wide variety of syntheses on the basis of 3-quinuclidone and they can be divided into two groups: (a) reactions with retention of the carbon chain length and (b) reactions involving an increase in the carbon chain length.

a. Reactions with retention of the carbon chain length. The hydrogenation of 3-quinuclidone and its substituted derivatives to the corresponding alcohols with subsequent esterification made it possible to synthesise a large number of esters and urethanes of 3-quinuclidinol, which are of considerable interest from the standpoint of the investigation of their biological activity [33,102,103,111,112,146-151]:

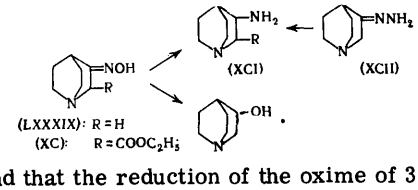


The Clemmensen[33] and Wolff–Kishner[152] reduction of 3-quinuclidone yields quinuclidine. The application of the Wolff–Kishner reaction to 2-substituted derivatives of 3-quinuclidone made it possible to obtain 2-substituted quinuclidine derivatives. Ethyl quinuclidine-2-β-propionate (LXXXVII)[104] and 2,6-dimethylquinuclidine (LXXXVIII)[11] were obtained in this way from the corresponding 3-oxo-derivatives (LXXXV) and (LXXXVI):



(LXXXV) (LXXXVII) (LXXXVI) (LXXXVIII)

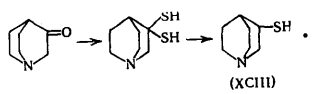
The oximes of 3-quinuclidone (LXXXIX)[103,122] and of ethyl 3-oxoquinuclidine-2-carboxylate (XC)[108] were reduced to the amines (XCI):



(LXXXIX): R = H
(XC): R = $COOC_2H_5$

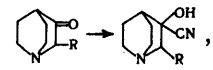
It was found that the reduction of the oxime of 3-quinuclidone (LXXXIX) in acid and neutral media is accompanied by hydrogenolysis and the reaction leads to the formation of 3-quinuclidinol together with 3-aminoquinuclidine (XCI, R = H). The reduction of the hydrazone of 3-quinuclidone (XCII) to 3-aminoquinuclidine takes place more unambiguously[122].

When 3-quinuclidone is treated with hydrogen sulphide and this is then followed by reduction with sodium tetrahydroborate, a sulphur-containing compound is produced—3-mercaptoquinuclidine (XCIII)[153]:

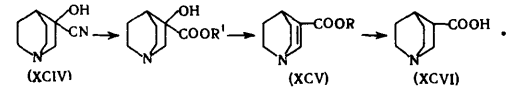


(XCIII)

b. Reactions involving an increase in the length of the carbon chain. The interaction of 3-oxo-derivatives of quinuclidine with potassium cyanide[109,121,154] or acetone cyanohydrin[122] was used to prepare cyanohydrins of the quinuclidine series:

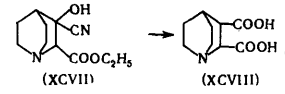


where R = H or $COOC_2H_5$. The hydrolysis of the cyanohydrin of 3-quinuclidone (XCIV) and subsequent dehydration led to the synthesis of 3-alkoxycarbonyl-Δ^2-dehydroquinuclidines (XCV), which were then reduced and hydrolysed to give quinuclidine-3-carboxylic acid (XCVI)[121,122]:



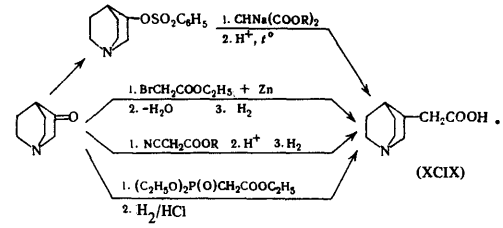
(XCIV) (XCV) (XCVI)

Quinuclidine-2,3-dicarboxylic acid (XCVIII) was obtained similarly from the cyanohydrin of 2-ethoxycarbonyl-3-quinuclidone (XCVII):[109]



(XCVII) (XCVIII)

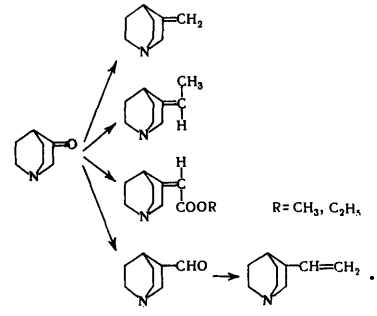
Various methods for incrementing the carbon chain were used to synthesise quinuclidine-3-acetic acid (XCIX):



(XCIX)

Comparison of different syntheses shows that the smallest yield of the acid (XCIX) is observed in sodiomalonic synthesis (13.4%),[125] much better results being obtained in the Reformatsky (40%)[125] and Knoevenagel condensations (65–70%):[126] a nearly quantitative yield can be achieved in the Wittig–Horner reaction[155].

The application of the Wittig–Horner reactions to 3-quinuclidone and other β-oxo-derivatives of quinuclidine[127,140,155-157] made possible the preparation of a wide variety of 3-substituted quinuclidines[128,140,157]:

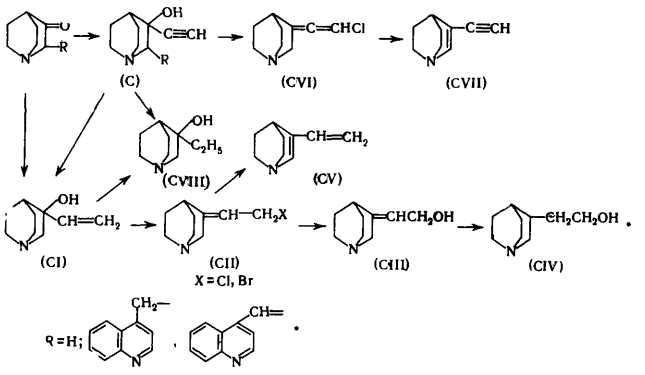


R = CH_3, C_2H_5

For example 3-methylene-, 3-ethylidene-[157], 3-alkoxycarbonylmethylene-[128], and 3-formyl-quinuclidines[140] have been synthesised by means of the above reactions. The reactions were found to be stereospecific[157]. In the synthesis of 3-ethylidenequinuclidine the ylide was found to attack predominantly from the sterically more favourable direction, when the methyl group in the transition complex is furthest removed from the 2 α-protons of the

quinuclidine ring. In the synthesis of 3-alkoxycarbonylmethylenequinuclidines the stereochemistry of the process was determined by the interaction of the nitrogen of the quinuclidine ring with the alkoxycarbonyl groups which led to the formation of only that geometrical isomer in which the above groups are close to one another.

Double application of the Wittig reaction initially with methoxymethylenetriphenylphosphorane and then with methylenetriphenylphosphorane led to the conversion of 3-quinuclidone into 3-vinylquinuclidine in two stages with an overall yield of 50%.[156] The above method for the introduction of the vinyl group into the β-position of the quinuclidine ring is of considerable interest, since various other synthetic procedures[36,37,158,159] either did not result in the formation of unsaturated quinuclidine compounds or involved the migration of the double bond to an exocyclic position. The introduction of an ethyne group into 3-quinuclidone[136,160] and its 2-substituted derivatives leads to 3-ethynyl-3-hydroxyquinuclidines, which are readily hydrogenated to 3-ethyl-3-hydroxyquinuclidines:

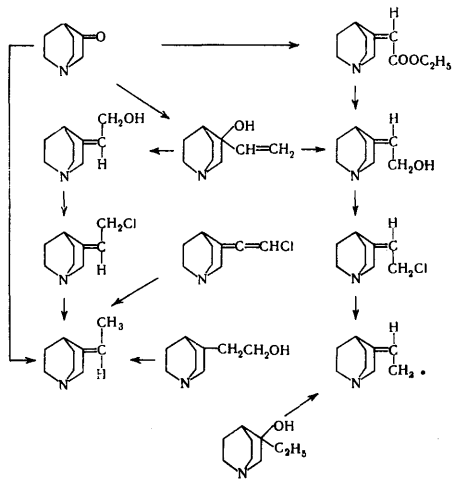


The selective reduction of 3-ethynyl-3-hydroxyquinuclidine, (C, R = H) led to the preparation of 3-hydroxy-3-vinylquinuclidine (CI)[136]. The latter was also synthesised directly from 3-quinuclidone and vinylmagnesium bromide[161].

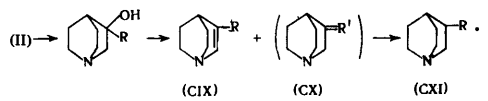
The substitution of the hydroxy-group in compound (CI) by a halogen with thionyl chloride or hydrobromic acid is accompanied by allyl rearrangement with formation of 3-(β-halogenoethylidene)quinuclidines (CII). 3-(β-Bromoethylidene)quinuclidine was converted via the 3-(β-hydroxyethylidene) derivative (CIII) into 3-(β-hydroxyethyl)-quinuclidine (CIV)[136] and then 3-vinyl-Δ²-dehydroquinuclidine (CV) was obtained by the dehydrohalogenation of 3-(β-chloroethylidene)quinuclidine[161].

Similar processes, associated this time with the acetylene–allene rearrangement were observed also when the hydroxy-group in 3-ethynyl-3-hydroxyquinuclidine (C, R = H) was replaced by a halogen. In this case the product was 3-(β-chloroallene)quinuclidine (CVI)[157] which readily eliminates hydrogen halide with formation of 3-ethynyl-Δ²-dehydroquinuclidine (CVII). The study of the allyl and acetylene–allene rearrangements in the series of 3-substituted quinuclidines[161] led to the determination of the effect of these processes on the positions of the multiple bonds in unsaturated quinuclidine compounds. In the course of these investigations it was shown that in the oxidation and ozonolysis of substances containing functional groups in the allyl position relative to the double bond not only the multiple but also the single C–C bonds adjacent to them are dissociated. For example, in the oxidation with potassium permanganate under mild conditions and in the ozonolysis of 3-hydroxy-3-vinylquinuclidine (CI), 3-quinuclidone is formed[161]. Therefore the position of multiple bonds in such allyl systems may be established unambiguously not with the aid of oxidative procedures but by analysing the NMR spectra[161].

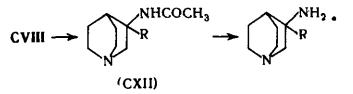
Two series of geometrical isomers of 3-substituted quinuclidines with a semicyclic double bond were synthesised by various reactions of 3-quinuclidone: 3-ethylidene[136,157,162], 3-(β-hydroxyethylidene)-[136,157], and 3-(β-chloroethylidene)-quinuclidines[157]; within each series interconversions were carried out[157] and the steric structure of the compounds was established with the aid of NMR spectra[16,157,163]:



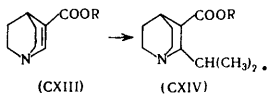
The interaction of 3-quinuclidones with organolithium or organomagnesium compounds is a general method for the synthesis of a large number of tertiary alcohols (CVIII)[47,162,164–168]. Their subsequent dehydration led to the formation together with Δ²-dehydroquinuclidines (CIX) of substances with an exocyclic double bond (CX)[165–168]. The reduction of the unsaturated products made it possible to obtain various 3-substituted quinuclidines (CXI):



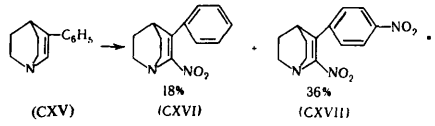
When 3-alkyl(aryl)-3-hydroxyquinuclidines (CVIII) were allowed to react with acetonitrile under the conditions of the Ritter reaction, acetylated 3-alkyl(aryl)-3-aminoquinuclidines (CXII) were obtained:



An interesting method for the introduction of substituents into the 2-position of the quinuclidine ring on the basis of 3-substituted Δ²-dehydroquinuclidines (CIX) has been described[47]. When methyl Δ²-dehydroquinuclidine-3-carboxylate (CXIII) reacts with isopropylmagnesium bromide, 1,4-addition takes place with subsequent formation, in the course of further treatment, of 2-isopropyl-3-methoxycarbonylquinuclidine (CXIV):

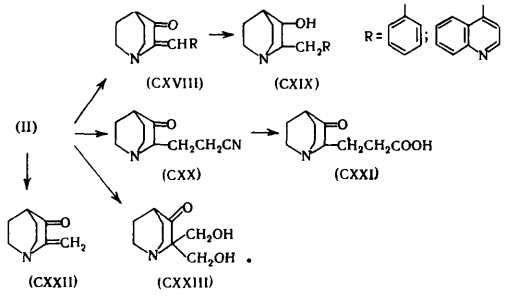


Unusual 2-substituted quinuclidines were obtained also on nitrating 3-phenyl-Δ^2-dehydroquinuclidine (CXV). The reaction products in this case proved to be 2-nitro-3-phenyl-Δ^2-dehydroquinuclidine (CXVI) and 2-nitro-3-(*p*-nitrophenyl)-Δ^2-dehydroquinuclidine (CXVII)[47]:



(CXV) (CXVI) (CXVII)

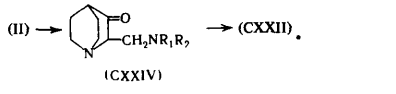
A number of 2-substituted quinuclidines were obtained by the condensation of 3-quinuclidone with aldehydes[77,103,109] and acrylonitrile[104]:



(CXVIII) (CXIX) (II) (CXX) (CXXI) (CXXII) (CXXIII)

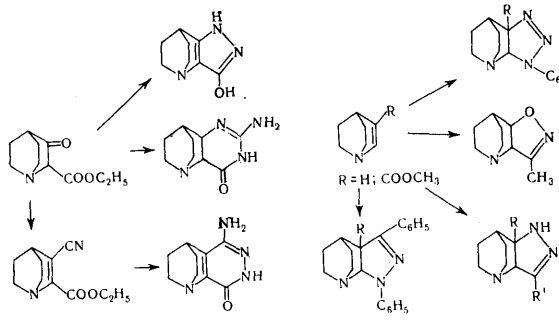
These reactions made it possible to convert 3-substituted quinuclidines into 2,3-disubstituted derivatives. For example 3-quinuclidone was converted via 2-[phenyl(quinolin-4′-yl)methylene]-3-quinuclidone (CXVIII) into 2-[phenyl-(quinolin-4′-yl)methyl]quinuclidin-3-ol (CXIX) and also into 2-(β-cyanoethyl)-3-oxoquinuclidine (CXX) and further into 3-oxoquinuclidine-2-β-propionic acid (CXXI). The formylation of 3-quinuclidone leads to the formation of 2-methylene-3-quinuclidone (CXXII) and, when a large excess of formaldehyde is employed, the product is a β-ketol—2,2-bishydroxymethyl-3-quinuclidone (CXXIII)[77].

2-Methylene-3-quinuclidone (CXXII) was also obtained by the Mannich reaction[170]. The 2-dialkylaminomethyl-3-quinuclidones (CXXIV) formed as intermediates in this case are converted into compound (CXXII) on distillation:



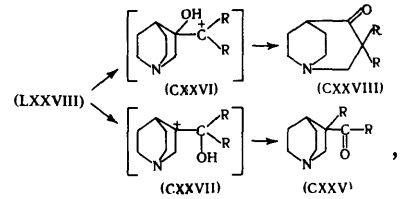
(II) (CXXIV) (CXXII)

Condensed heterocyclic systems containing the quinuclidine ring (pyrazolo-, oxazolo-, triazolo-, pyrimidino-, and pyridazino-quinuclidines[171]) were synthesised from ethyl 3-oxoquinuclidine-2-carboxylate (CXXXV) and also from Δ^2-dehydroquinuclidine and methyl Δ^2-dehydroquinuclidine-3-carboxylate obtained from 3-quinuclidone:



3. REACTIONS INVOLVING THE EXPANSION OF THE QUINUCLIDINE RING

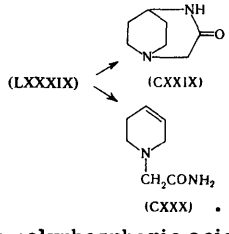
The study of the pinacol rearrangement of ditertiary quinuclidine alcohols of the type of compound (LXXVIII)[144,172] showed that, depending on the nature of the substituents R and the reactants employed, the process takes place either with ring expansion or with the formation of ketones of the quinuclidine series [compounds (CXXV)]:



(LXXVIII) (CXXVI) (CXXVIII) (CXXVII) (CXXV)

where R = CH_3, C_4H_9, C_6H_5, or *p*-$CH_3C_6H_4$. This is associated with the possible reaction via two types of carbonium ions [(CXXVI) and (CXXVII)] with electrophilic centres at the C_3 atom of the quinuclidine ring or at the carbon atom of the side chain respectively. The subsequent migration of the aryl or alkyl group leads in the first case to ketones of the quinuclidine series (CXXV) and the migration of the methylene group in the second case leads to the formation of 4-oxo-derivatives of 1-azabicyclo[3,2,2]nonane (CXXVIII). For aryl substituents, stabilisation is achieved as a result of the conjugation of carbonium ions of type (CXXVI). Therefore, on treatment with sulphuric acid, 3-($\alpha\alpha$-diaryl-α-hydroxymethyl)-3-hydroxyquinuclidines (LXXVIII, R = Ar) are more readily converted into compounds (CXXVIII) than the analogous 3-($\alpha\alpha$-dialkyl-α-hydroxymethyl)-3-hydroxyquinuclidines (LXXIII, R = Alk). The use of an aprotic reagent, zinc chloride in acetic anhydride, yields carbonium ions (CXXVII) as a result of the elimination of an acetate ion from the initially formed monoacetyl derivatives of the glycols (LXXVIII). Therefore in aprotic media expansion of the quinuclidine ring does not take place and the reaction leads to ketones of the quinuclidine series (CXXV) or dehydration and acylation products of the initial glycols.

The Beckmann rearrangement of the oxime of 3-quinuclidone (LXXXIX) in the presence of polyphosphoric acid or oleum takes place with expansion of the quinuclidine ring and the formation of 3-oxo-1,4-diazabicyclo[3,3,2]nonane (CXXIX)[173,174]:



(LXXXIX) (CXXIX) (CXXX)

In the reaction with polyphosphoric acid the intermediate cation is stabilised after the dissociation of the C_3–C_4 bond not only by the formation of a new C–N bond but also by the elimination of the proton from C_5. In the latter case a product resulting from the opening of the quinuclidine ring is formed: the amide of Δ^3-dehydropiperidine-*N*-acetic acid (CXXX).

The same products of quinuclidine ring expansion or opening arise also on treatment of 3-quinuclidone with hydrazoic acid under the conditions of the Schmidt reaction[175]. However, in the latter case the process is largely displaced towards the monocyclic amide (CXXX).

When the oxime of 3-quinuclidone reacts with arenesulphonyl chlorides in an alkaline medium, *N*-substituted 4-cyanopiperidines are formed[176,177].

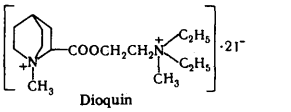
IV. BIOLOGICAL PROPERTIES OF QUINUCLIDINE DERIVATIVES

There have been mainly two aspects to the study of the biological properties of quinuclidine derivatives: on the one hand natural alkaloids, their synthetic analogues, and reaction products were investigated and on the other the characteristics of the pharmacological activity of compounds associated with the presence of the quinuclidine ring were elucidated. In the present review it is probably useful to consider only the investigations of the second type, since, as mentioned above, a number of reviews are available on the biological activity of the quinuclidine alkaloids.

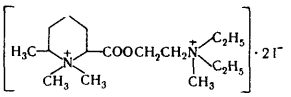
The first study on the pharmacological activity of unsubstituted quinuclidine was carried out by Stern in 1941.[178] In experiments on animals, it was shown that the hydrochloride of unsubstituted quinuclidine exhibits appreciable hypotensive activity and relaxes the smooth musculature, while the corresponding quaternary ammonium salts show a curare-like activity. In the course of subsequent systematic studies of quinuclidine and other 1-azabicycloalkane derivatives in the USSR under the direction of M. V. Rubtsov, synthetic methods were developed and a large number of compounds of this series were obtained and subjected to biological tests. The study of the pharmacological properties of quinuclidine and other 1-azabicycloalkane derivatives carried out under the direction of M. D. Mashkovskii revealed the high activity of compounds of this kind and led to the discovery of effective medicinal preparations, which have found application in medical practice[130,179-182].

The experimental investigation of aminoalkyl esters of quinuclidinecarboxylic acids and their halogenoalkylate derivatives and also tertiary amines of the 2- and 3-monosubstituted and 2,3-disubstituted quinuclidine series led to the discovery of preparations which interfere with the transmission of nervous excitation in ganglia[130,183]. Thus ethyl quinuclidine-3-carboxylate shows a nicotine-like activity and 2-diethylaminoethylaminomethylquinuclidine and other similar tertiary amines suppress the excitation in ganglia. The most active ganglion-blocking agents proved to be the quaternary derivatives of dialkylaminoethyl esters of quinuclidine-2- and quinuclidine-3-carboxylic acids. The di-iodomethylate of the diethylaminoethyl ester of quinuclidine-2-carboxylic acid (CXXXI), which was called Dioquin, is one of the most powerful modern ganglion-blocking agents[184-188]. Substances with similar activity, namely the di-iodomethylate of the dimethylaminoethyl ester of quinuclidine-3-carboxylic acid and the di-iodomethylate of the dimethylaminoethyl ester of quinuclidine-2-carboxylic acid, i.e. the dimethyl analogue of Dioquin, are three times more active than Dioquin itself. In subsequent studies of the relation between chemical structure and biological activity it was established that the ganglion-blocking activity persists on going over from the bicyclic quinuclidine system to the monocyclic piperidine system: the di-iodomethylates of the dimethylaminoethyl (CXXXII) and diethylaminoethyl (CXXXIII) esters of 1,6-dimethylpipecolic acid, called Dimecoline and Dicoline[189-196], have been introduced into the medical practice in the USSR as active ganglion-blocking agents for the treatment of hypertonia, stomach ulcers, bronchial asthma, and many other diseases. The introduction into the molecule of the active compound of various branched dialkylaminoalkyl chains instead of the dialkylaminoethyl substituents lowers the ganglion-blocking activity of these substances[197].

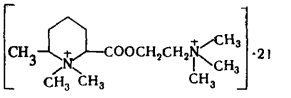
It is interesting to note that the ganglion-blocking activity of secondary-tertiary amines of the type of 2-benzylaminomethyl-3-(β-benzylaminoethyl)quinuclidine (CXXXIV) is closely associated with the presence of the bicyclic quinuclidine system in the molecule in contrast to the analogous activity of the quaternary salts of aminoalkyl esters of quinuclidinecarboxylic acid. In this case, on going over to compounds without the quinuclidine ring, the effect on the ganglia of the vegetative nervous system disappears.



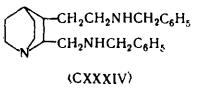
Dioquin
(CXXXI)



Dicoline
(CXXXIII)

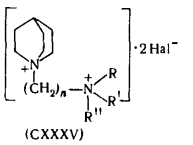


Dimecoline
(CXXXII)

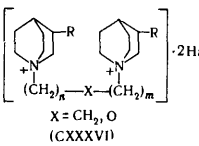


(CXXXIV)

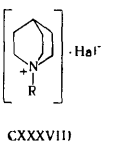
In the search for ganglion-blocking and curare-like preparations diquaternary salts in which one [as in compound (CXXXV)][198,199] or both [as in compound (CXXXVI)][200-202] quaternary nitrogen atoms linked by the alkylidene chain are constituents of the quinuclidine ring were synthesised and tested together with 1-alkylquinuclidinium halides[203] (CXXXVII, R = Alk) and *N*-aminoquinuclidinium salts (CXXXVII, R = NH_2)[204]:



(CXXXV)

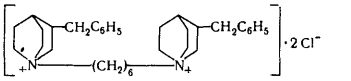


X = CH_2, O
(CXXXVI)



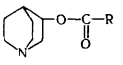
CXXXVII)

The most pronounced curare-like properties were found in the dichloride of 1,6-di-(3′-benzylquinuclidin-1′-yl)hexane (CXXXVIII), which has been introduced in the USSR medical practice under the name of Qualidyl[200,202] as a curare-like preparation with a competitive activity:

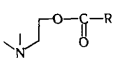


Qualidyl
(CXXXVIII)

The esters of 3-hydroxyquinuclidine (CXXXIX), which are bicyclic analogues of the esters of 2-dialkylaminoethanol (CXL), were found to have interesting pharmacological properties:



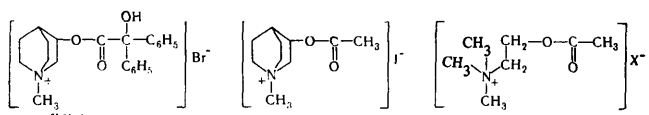
(CXXXIX)



(CXL)

Many esters formed by 2-dialkylaminoethanols with various carboxylic acids are known to have neurotropic properties. The first studies by Sternbach, Kaiser, and coworkers[103,146-148,164] already showed that the esters of 3-hydroxyquinuclidine and aromatic acids (benzilic, tropic, etc.) caused the relaxation of the smooth musculature.

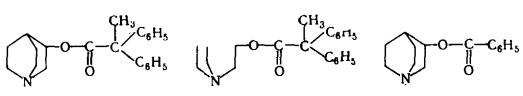
Almost at the same time Duschinsky[149] showed that carbamic esters of 3-hydroxyquinuclidine have a similar effect. The bromomethylate of the benzilate of 3-hydroxyquinuclidine (CXLI), called Clidinium bromide (Quartzan bromide or Marplan) has found application in the medical practice of the USA and of many other countries as a cholinolytic agent[205-211]:



clidinium bromide

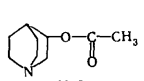
(CXLI) (CXLII) (CXLIII)

A systematic study of the pharmacological properties of the esters of 3-hydroxyquinuclidine and related compounds was carried out by Mashkovskii and coworkers[179,180]. In the first place the iodomethylate of 3-acetoxyquinuclidine (CXLII), which is a bicyclic analogue of acetylcholine (CXLIII), was investigated. The compound exhibited a cholinomimetic activity but its action was weaker than that of acetylcholine. The corresponding tertiary amine, 3-acetoxyquinuclidine, which, in contrast to acetylcholine, shows a more selective effect on muscarine receptors and readily penetrates through the haematoencephalic barrier, is an effective cholinomimetic agent. The salicylate of 3-acetoxyquinuclidine (CXLIV), called Aceclidine[181,212,213] is used in the USSR and a number of other countries in ophthalmology for the treatment of glaucoma and also in surgical and obstetric and gynaecological practice as a means of combating postoperative atonia of the organs in the abdominal cavity, including the postnatal atonia of the mother. Further studies showed that the cholinomimetic activity of Aceclidine is to a considerable degree associated with the presence in the molecule of the quinuclidine ring[151,214,215] and the replacement of 3-hydroxyquinuclidine and other similar bicyclic or monocyclic amino-alcohols results in a reduction or complete loss of activity:



aprolidine (CXLV) aprophene (CXLVI) oxilidine (CXLVII)

The cholinomimetic activity also falls when an alkyl group is introduced in the 6- and 8-positions of the quinuclidine ring. The replacement of the acetyl group in Aceclidine by the residues of homologous aliphatic acids leads initially to a decrease of the cholinomimetic activity (propionic ester) and then to the appearance of cholinolytic properties (butyric and isovaleric esters). The esters of 3-hydroxyquinuclidine and aliphatic–aromatic acids are also powerful cholinolytic agents. For example, the diphenylpropionate of 3-hydroxyquinuclidine (CXLV) (Aprolidin)[216-218] greatly surpasses[219] in its effect on the central and peripheral choline-reactive systems the analogous ester of 2-diethylaminoethanol (CXLVI) [known in the USSR as Aprophen]:



$C_7H_6O_3$

Aceclidine

(CXLIV)

The esters of 3-hydroxyquinuclidine with aromatic acids have a calming effect on the central nervous system. For example, the hydrochloride of 3-benzoyloxyquinuclidine (CXLVII), employed in the USSR under the name of Oxylidine[182,220-226] has a very pronounced sedative activity. Oxylidine is particularly effective in nervous breakdowns associated with the failure of blood circulation in the brain. At the same time Oxylidine also exhibits a hypotensive activity and has found application in the therapy of hypertonia. It is noteworthy that, as in the case of Aceclidine, the high biological activity of other 3-hydroxyquinuclidine esters is also associated with the presence in their molecules of the azabicyclic quinuclidine system. This is confirmed by the weakening of the pharmacological activity in the corresponding esters of 3-hydroxypiperidines and the esters of the completely open-chain type related to 3-hydroxyquinuclidine (*N*-alkyl-*N*-cycloalkylaminoethanols) and also by the lowering of pharmacological activity on going over to analogous esters of other 1-azabicycloalkanols. Possibly the higher activity of 3-hydroxyquinuclidine derivatives, compared with that of the analogous derivatives of other mono- and bi-cyclic amino-alcohols is associated with the characteristics of the quinuclidine molecule, noted above, in which the unshared electron pair of the nitrogen atom is not hindered.

The more ready interaction of the free electron pair of the nitrogen atom in the quinuclidine ring with electrophilic centres of the corresponding receptors in the organism is responsible, according to some workers[227], for the higher psychotropic activity of the benzilic esters of 3-hydroxyquinuclidine compared with the esters of other *N*-substituted amino-alcohols. The low probability of intramolecular bonds and interactions in 3-hydroxyquinuclidine esters, where the acyl component of the molecule and the free electron pair of the nitrogen atom are oriented in different directions, has also been noted. Probably further studies will lead to a more complete elucidation of the effect of the characteristics of the chemical behaviour of the quinuclidine molecule, its conformation, the nature of the free electron pair of the nitrogen atom, etc. on the physiological activity of various quinuclidine derivatives and will lead to the discovery of new active compounds.

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Ordzhonikidze All-union Institute of Chemopharmacology, Moscow

U. D. C. 547.387

Ketens *in situ* and Cycloaddition to Them

F.I.Luknitskii and B.A.Vovsi

The review deals with the methods of generation of ketens *in situ*, particularly their reaction behaviour, mainly in cycloaddition to compounds containing multiple bonds. The ways in which ketens are polymerised *in situ*, associated both with the structure of the ketens themselves and the methods of their preparation, are also discussed. The bibliography incorporates 102 references.

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1. INTRODUCTION

More than 60 years have elapsed since the first mention of ketens in papers by Wilsmore[1] and Staudinger and co-workers[2], and yet at present only a few stable representatives of this class of compound have been isolated in a pure state: keten itself, dimethyl-, diphenyl-, and perfluoro-dimethyl-ketens, and certain others. Monosubstituted ketens are particularly difficult to prepare.

At the same time the number of ketens which have not been characterised in a free state but are used as intermediates (*in situ*) is much greater. Because of their high reactivity, ketens are of considerable interest for organic synthesis both in the laboratory and in industry. For this reason, several reviews have been devoted to the chemistry of ketens (mainly to the simplest of them)—the reviews of Lacey[3], Kagan[4], and somewhat earlier Hanford and Sauer[5] and Quadbeck[6]. A recent review by Dashkevich and Beilin was devoted to the chemistry of carbon suboxide.

However, none of the authors enumerated above dealt with the problem of the reactivity (and also a systematic account of the data concerning the methods of generation) of ketens *in situ*, which sometimes differs from the reactivity of ketens isolated in a pure state even in the same reactions.

The aim of the present review is to give a general account of the literature information (up to 1967 inclusive) on the methods of generation of ketens *in situ* and their participation in cycloaddition reactions†. The review is restricted to only this type of reaction because it is precisely in these reactions that the specific reactivity of keten *in situ* is shown most markedly. In this connection di- and tri-merisation are also discussed, but the reactivity of the dimers themselves, which has been described fairly completely in the available reviews on the chemistry of diketen, is consistently disregarded.

An exception to this principle is made in the present review only under discussion of the mechanism of addition to ketens (including ketens *in situ*) where it is possible for a better understanding of the problem to give a more general account also of certain other addition reactions of ketens apart from cycloaddition.

† The term "cycloaddition" is employed by the present authors in view of its wide use in the chemical literature, instead of the term "cycloformation" which they believe to be more correct.

We also believe it to be desirable to restrict the discussion of ketens formed as intermediates as a result of the Wolff rearrangement[8] in the photolysis and thermolysis of diazo-carbonyl compounds exclusively to reactions involving cycloaddition to these ketens *in situ*, particularly since, when the Wolff rearrangement is carried out in an aprotic medium, certain ketens can be isolated and characterised in a pure form[9,10].

The review also does not deal with the structural analogues of ketens, for example sulphenes *in situ*, the chemistry of which was dealt with in a recent review by Opitz[11].

2. METHODS OF GENERATION OF KETENS IN SITU

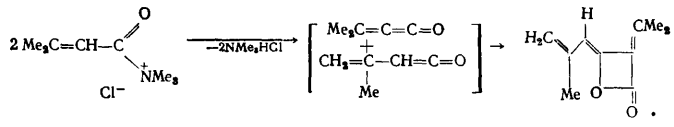
One of the early and most widespread methods for the generation of ketens *in situ* is the elimination of hydrogen halides from acid halides with a hydrogen atom in the α-position under the action of strongly basic tertiary amines[12,13]:

$$\text{>CH—C(=O)Cl} + \text{Alk}_3\text{N} \rightarrow [\text{>C=C=O}] + \text{Alk}_3\text{NHCl}.$$

However, this method has not been used for a long time, since initially only diphenylketen could be isolated in monomeric form and used further for preparative purposes. Other ketens formed by this method underwent di- and tri-merisation before isolation. Only in recent years have attempts been resumed to find preparative applications of ketens *in situ* using various "intercepting" components. By dehalogenating the halides of mono- and di-substituted acetic acid, it proved possible to generate and introduce into further reactions many ketens which have not been described in a pure state. For example, after unsuccessful attempts by Staudinger[14] to isolate dichloroketen by the thermolysis of dichloromalonic anhydride, there was no further information in the literature about the participation of this keten in any reactions until in 1965 Stevens et al.[15] obtained dichloroketen as an intermediate from dichloroacetyl chloride and a trialkylamine in the presence of cyclopentadiene as an "interceptor" of keten *in situ*. Hull obtained difluoroketen by a similar procedure[16]. Since this method of generation of ketens *in situ* has been extended to reactions of tertiary amines with acid dichlorides of the type $ClCO-(CH_2)_n-COCl$, the intermediate bisketens also became available[17-21].

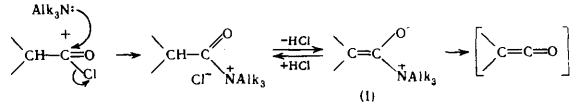
The intermediate formation of ketens in the interaction of tertiary amines with the chlorides of $\alpha\beta$-unsaturated

acids is unlikely, since in this case the α-hydrogen atom is by no means as labile as in substituted acetylchloride. Nevertheless the formation of a β-lactone in the solvolysis of a quaternary salt obtained from the chloride of dimethylacrylic acid and trimethylamine is evidence, according to Payne[22], of the intermediate formation of ketens, which are then further dimerised:



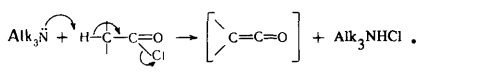
The mechanism of the interaction of acid chlorides with tertiary amines has not been the subject of a special investigation. However, since it proved possible to isolate the adducts of acid halides with weakly basic tertiary amines (pyridine, *NN*-dialkylanilines, etc.), it was suggested[13], by analogy, that the reaction of acid halides with strongly basic amines also involves the formation of a quaternary salt of the type $Alk_3\overset{+}{N}COR\,Cl^-$.

According to Pracejus[23], keten is formed from this quaternary salt via an intermediate dipolar compound (I) of keten with trialkylamine:



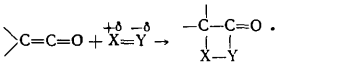
(I)

This mechanism of the formation of intermediate ketens from quaternary ammonium salts, analogous to the Hofmann degradation, is one of several which are possible. On the other hand, intermediate ketens can be obtained also without the preliminary formation of quaternary salts from acid chlorides and amines—by an E_2 bimolecular elimination mechanism:

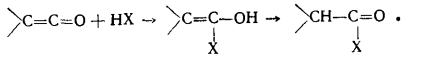


The problem of which of these two mechanisms actually occurs in the interaction is important for the elucidation of the mode of the secondary process—the addition of the "interceptor" reagent to the C=O or C=C bond of the intermediate keten, provided a stabilised keten is not formed in the reaction.

Nevertheless this aspect too remained fairly obscure for a long time, i.e. as regards the mode of reactions involving additions to stable ketens. Most investigators regarded the addition to the C=C bond of ketens and the addition to the C=O bond with subsequent isomerisation to the product of addition to the C=C bond as equally probable[24-26]. Mueller[27], who summarised the various views, suggested that reagents containing multiple bonds (C=C, C=O, C=N, N=N,) etc., add to ketens at their C=C bond with formation of cycloadducts:

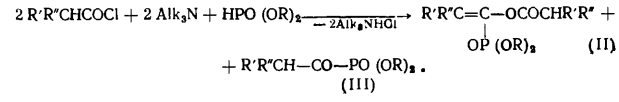


Reagents without multiple bonds, mainly substances with a mobile hydrogen atom (water, amines, alcohols, acids) add to ketens at their carbonyl group with possible (but not obligatory) subsequent isomerisation of the vinyl alcohol to a carbonyl derivative:



In some cases it is possible to acylate the intermediate vinyl alcohol by a second keten molecule, whereupon of course isomerisation does not occur. Hydrocyanic acid[28], Gringard reagents[29], lithium tetrahydroaluminate[30], and dialkyl phosphites[31,32] add to the carbonyl group of keten in this way.

The intermediate ketens from acid chlorides and tertiary amines probably also enter into addition reactions both at the C=C and C=O bonds. For example, addition to the C=O bond is observed in the interaction of dialkyl phosphites with mono- and di-substituted acetyl chlorides in the presence of triethylamine[33]:



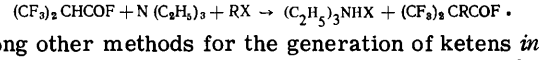
(II)

(III)

When R′ = R″ = H and R = CH_3, the yields of compounds (II) and (III) are 70 and 16% respectively. The formation in this case of α-oxophosphonic esters (III) together with the acyloxyvinyl adduct (II) can be explained both by addition to the C=C bond of the intermediate keten *in situ* and by the isomerisation of the vinyl alcohol derivative, which may occur at the same time as the acylation of the hydroxy-group of a second keten molecule *in situ*; finally, the formation of compounds (II) and (III) may be caused by the difference in the rates of addition of the vinyl alcohol derivative and dialkyl phosphite to the C=C bond of a keten *in situ*.

Although the method of generation of ketens *in situ* discussed has found wide application, it is not universal. Unsuccessful attempts to intercept many potential ketens without their preliminary isolation from the reaction mixture can probably be explained by the short lifetime of the intermediate ketens in monomeric form or by the low rate of interception of ketens *in situ*, as a result of which the principal reaction products are often resinous oligomers or at best keten dimers and trimers.

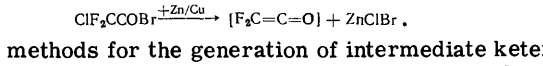
The fluoride of hexafluoroisobutyric acid reacts with triethylamine in quite a different way[34]. Neither the hydrofluoride of triethylamine, nor perfluorodimethylketen (known in a pure state), nor the product of its oligomerisation are formed, fluorophosgene and a complex adduct with the amine being isolated. In the presence of an alkyl halide RX, the corresponding triethylammonium halide is obtained, but not the fluoride, the formation of which might confirm indirectly the intermediate generation of the keten:



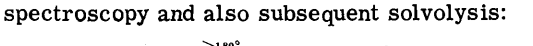
Among other methods for the generation of ketens *in situ*, the dehalogenation of α-halogeno-acid halides, for example with the aid of zinc activated with copper[35-37], is of practical interest. The bromides of trihalogenoacetic acids in a solvent inert with respect to ketens (ether, ethyl acetate) enter into this reaction most readily:

where X = Cl[35], or Br[36].

Difluoroketen, which is intercepted with ammonia *in situ* to avoid oligomerisation[37], was obtained similarly:

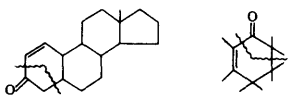


Other methods for the generation of intermediate ketens with interception *in situ* are also known. For example, Ziegler and Sterk[38] confirmed the intermediate formation of ketens in the thermolysis of β-diketones with the aid of infrared spectroscopy and also subsequent solvolysis:



Ziegler et al.[30] also suggested the intermediate formation of ketens in the dehydration of benzylmalonic acid with acetic anhydride.

The formation of ketens following the electron bombardment of conjugated cyclohexenones has been observed mass-spectrometrically[40] (the wavy line indicates the keten fragment formed):



According to Schneibaum[41], the oxidation of certain acetylenes with nitrobenzene is accompanied by the intermediate formation of ketens, which are intercepted *in situ* by solvolysis:

$$C_6H_5NO_2 + -C\equiv C- \rightarrow C_6H_5NO + \left[\rangle C{=}C{=}O\right] \rightarrow \text{solvolysis products.}$$

A "keten" mechanism has also suggested[42] for the reaction of substituted acetylenes with per-acids; according to this view, the hypothetical acetylene α-oxide rearranges to a keten, which undergoes solvolysis *in situ*:

$$RCO{-}OOH + -C\equiv CR' \rightarrow \underset{\diagdown O \diagup}{-C=\!=C-R'} \xrightarrow{H^+} \left[R'{-}\underset{|}{C}{=}C{=}O\right].$$

We believe that the intermediate formation of ketens in this reaction can be explained also in a different way—by the oxidation of acetylene to alkyn-1-ol with subsequent El'tekov rearrangement:

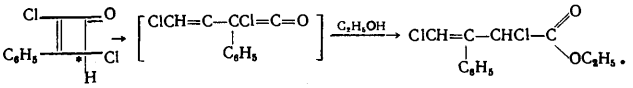
$$RCO{-}OOH + -C\equiv C{-}R' \rightarrow HO{-}C\equiv C{-}R' \rightarrow [O{=}C{=}CH{-}R'].\quad ‡$$

Such a mechanism can explain satisfactorily the intermediate formation of monosubstituted ketens only, while the mechanism proposed by Stille and Whitehurst[42] is suitable also for disubstituted ketens *in situ*.

Richard[43] suggested the intermediate generation of a keten to account for the conversion of α-halogeno-ketones into acids in the course of the Favorskii rearrangement:

$$ArCHClCOR \rightarrow [ArRC{=}C{=}O] \xrightarrow{H_2O} ArRCHCOOH.$$

In the alcoholysis of optically active dichlorophenylcyclobutenone, Jenny and Roberts[44] isolated a racemic ester:

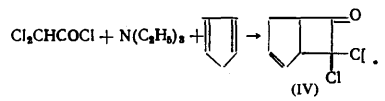


They explained the racemisation by the intermediate formation of a keten in which the asymmetric carbon atom of the initial keten ceases to be asymmetric by virtue of its transition to an sp^2-hybridised state.

3. CYCLOADDITION OF KETENS *IN SITU*

a. Cycloaddition to the C=C Bond

Activated olefins, for example, cyclic dienes are used as a rule to intercept ketens *in situ*. Products of 1,2-cycloaddition are then formed in high yield. Thus the intermediate formation of dichloroketen from dichloroacetyl chloride and triethylamine was confirmed for the first time, and the use of cyclopentadiene[15] as an "interceptor" permitted the synthesis of 7,7-dichlorobicyclo[3,2,0]hept-2-en-6-one(IV)



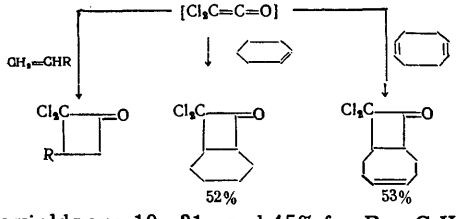
Further reactions of compound (IV) led to a new synthesis of tropolone.

The corresponding bicyclic dibromo-analogue was synthesised[36] similarly, both dehalogenation of tribromoacetyl bromide with zinc and the reaction of dibromoacetyl chloride with triethylamine being used for the generation of the intermediate dibromoketen.

Monosubstituted intermediate ketens add *in situ* to cyclic dienes by the same mechanism[45].

Non-activated olefins also react with ketens *in situ* forming cyclic products, electrophilic substituents in the keten molecules favouring its interception by the olefin.

For example, dichloroketen reacts more vigorously *in situ* than does dimethylketen under the same conditions. Cyclopentene[46], cyclohexene[47], cyclo-octadiene[47], styrene[47], and ethyl vinyl ether[47] are used as "intercepting" agents. In all cases cyclobutanones are formed. The yields of the corresponding reactions involving the interception of dichloroketen *in situ* are given below:

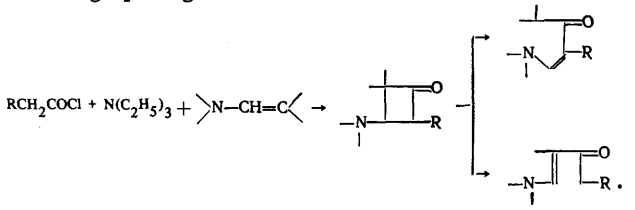


where the yields are 19, 31, and 45% for R = C_6H_5, C_3H_7, and OC_2H_5 respectively.

The choice of the method of generation of intermediate ketens in the presence of olefins is determined both by the nature of the olefin and the activity of the keten and the duration of its existence as a monomer. In the case of olefins which are not polymerised in the presence of zinc halides, the method of generation of ketens *in situ* by the dehalogenation of α-halogeno-acid halides is suitable. Otherwise, for example, when vinyl ethers are used as interceptors for ketens *in situ*, the method of generation based on the reaction of substituted acetyl chlorides with trialkylamines is more convenient, provided of course that the ketens themselves are not polymerised *in situ* in the presence of the amine and (or) its hydrochloride at a rate comparable to the rate of interception[5,47].

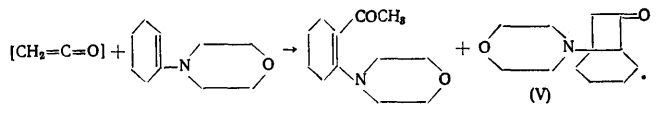
It has been mentioned[48] that the addition of dichloroketen *in situ* to indene (in a yield of 12%) leads to the formation of the corresponding 4,5-benzotropolone as a result of further reaction of the adduct.

Enamines add to aldoketens *in situ* with formation of β-aminocyclobutan-2-one derivatives which can be converted, under the reaction conditions, into acyclic amide vinylogues with ring opening:



‡ $RCO{-}OOH + -C\equiv C{-}R' \rightarrow H{-}O{-}\overset{H^+}{C}\equiv C{-}R' \rightarrow [O{=}C{=}CH{-}R']$ (Ed. of Translation).

In the reactions of ketens *in situ* with 1-morpholinocyclohexene (as the interceptor), the presence in the reaction mixture of a bicyclic addition product (V) has been confirmed[49] by infrared spectroscopy, but 2-acetyl-1-morpholinocyclohexene was isolated as the main product:

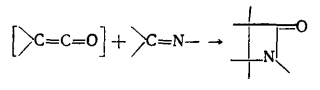


(V)

b. Cycloaddition to Multiple Carbon–Nitrogen Bonds

The addition of stable ketens to reagents containing a double or triple carbon–nitrogen bond can be achieved successfully only under very severe conditions and only a highly polarised C=N bond takes part in the reaction.

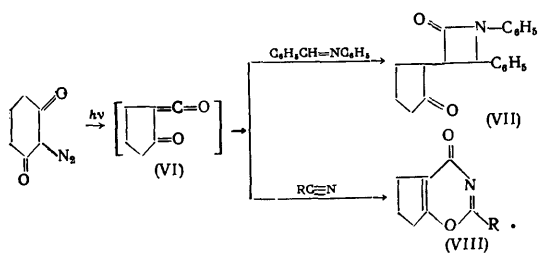
In contrast, ketens *in situ* add to both C=C and C=N bonds under mild conditions with formation of cyclic products. The addition of intermediate ketens to azomethines leads to the formation of β-lactans[50]:



The synthesis of β-lactams by cycloaddition to ketens *in situ* has been widely investigated[51-54] in connection with its employment for the synthesis of penicillins, the molecules of which contain condensed β-lactam rings. The chlorides of phthaloyl and succinyl glycine, which are introduced into the reaction with triethylamine in the presence of the corresponding azomethines, are used as a source of ketens in this case.

The photolysis of β-diazocarbonyl compounds[55] is also used for the synthesis of α-lactams via ketens *in situ*[55]. It has been noted that ketens with electronegative substituents (for example, *p*-chloro- and *p*-nitro-phenylketens) enter into the cycloaddition reaction at the C=N bond of the intercepting agent either with difficulty or do not react at all (in contrast to the effect of substituents of the same type on the cycloaddition of ketens *in situ* to olefins).

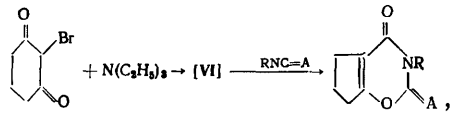
Intermediate α-oxoketens have a marked tendency to undergo 1,4-cycloaddition of reagents with multiple bonds[56], but in the reaction with anils 1,2-cycloadducts are nevertheless formed, albeit in a low yield. For example, β-oxoketen (VI) reacts *in situ* with benzylidene-aniline, forming a β-lactam(VII):



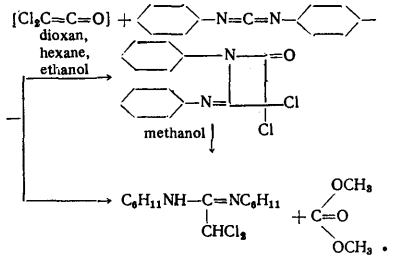
(VI) (VII) (VIII)

On the other hand, in the reaction of the keten (VI) *in situ* with nitriles a 1,4-cycloaddition product is formed—a condensed oxo-1,3-oxazine (VIII).

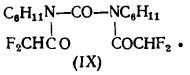
The reactions of the intermediate keten (VI) with isocyanates and isothiocyanates has been investigated by Selvarajan et al.[57], ketens being generated *in situ* by the reaction of triethylamine with 2-bromocyclohexa-1,3-dione;



where A = O or S, and



Difluoroketen reacts *in situ* with carbodi-imide forming acylated dicyclohexylureas (IX)[16]:



(IX)

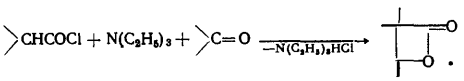
In this case the 1,4-cycloaddition product is obtained in a yield of the order of 25%.

Hull[16] noted that carbodi-imides add to ketens *in situ* with the cleavage of only one C=N bond; if the process is carried out in boiling dioxan, hexane, or ethanol the 1,1-adduct is a β-lactam, but if the solvent is methanol the final reaction product is a substituted dichloroacetamidine produced, according to the author, as a result of the solvolysis of the β-lactam formed initially.

c. Cycloaddition to the Carbonyl Group

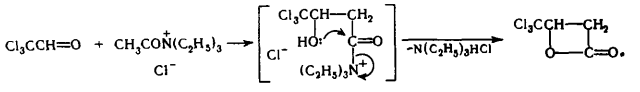
Stable ketens add to the carbonyl group of aldehydes and ketones with formation of β-lactones. These reactions take place only in the presence of various catalysts, which polarise the carbonyl group of the aldehyde or ketone. As a rule such catalysts are Lewis acids[3,58-61]. Evidently catalysts of this type are unsuitable for the reactions *in situ* of aldehydes or ketones with ketens generated by the action of trialkylamines on acid chlorides, since the Lewis acids would be immediately neutralised by the amines. Therefore, in the synthesis of β-lactones via ketens *in situ*, generated in this way, only highly polarised carbonyl components which do not require additional activation by a catalyst are employed as interceptors.

Thus β-trichloromethyl-β-propiolactone was synthesised[62] in 92% yield from acetyl chloride, triethylamine, and chloral. The replacement of acetyl chlorides by methanesulphonyl chloride made it possible to synthesise the corresponding β-sultone derivative[63]. Borrmann and Wegler[64] showed that this synthesis of β-lactones is general. The authors used the chlorides of acetic, dichloroacetic, and ring-substituted phenoxyacetic acids for the generation of the intermediate ketens and polyhalogeno-substituted aldehydes and ketones as intercepting agents:



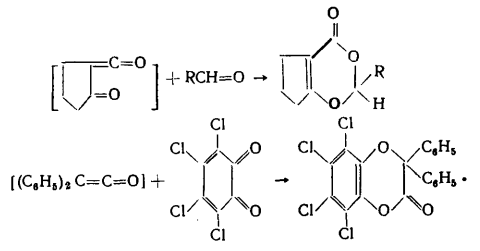
When optically active highly basic tertiary amines (for example brucine) are used for the generation of ketens *in situ*, it is possible to obtain[65] optically active β-lactones with one or two asymmetric carbon atoms.

Although at first sight the "keten" mechanism of the synthesis of β-lactones from substituted acetyl chlorides and tertiary amines in the presence of carbonyl intercepting agents appears to be the most likely, we believe that this process can also be explained in a different way[66], omitting the intermediate generation of the keten. Thus it may be supposed that the quaternary salt formed by reaction of the amine with the acid chloride, which has a hydrogen atom with enhanced lability in the α-position relative to the carbonyl, adds initially to the highly polarised carbonyl group of the intercepting agent; subsequently the alcoholic hydroxyl is acylated intramolecularly with the elimination of triethylamine hydrochloride and the closure of the β-lactone ring (shown below in the synthesis of β-trichloromethyl-β-propiolactone as an example:



This mechanism is supported, for example, by the fact that the yield of diketen in this reaction is negligible, becoming zero at sufficiently high dilution. Nevertheless, as will be shown below, the dimerisation of ketens *in situ* is strongly catalysed by tertiary amines and their salts. This should undoubtedly result in a decrease of the yield of β-lactone if an intermediate keten forms in the reaction. On the other hand, the absence from the reaction medium of diketen as a side product can be accounted for by the lower rate of its formation from the keten *in situ* compared with the rate of interception of the latter by the carbonyl compound. This view is confirmed by the finding that the yields of other β-lactones (except β-trichloromethyl-β-propiolactone) are not so high[64] although the formation of keten dimers as side products is not reported.

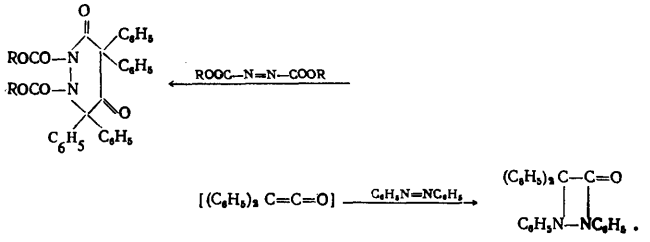
So far there is no convincing evidence in favour of any one of the mechanisms of the synthesis of β-lactones from acid halides, trialkylamines, and carbonyl compounds discussed above. On the other hand, when other methods are used for the generation of intermediate ketens in the presence of carbonyl compounds, β-lactones are not formed. Thus, when ketens are generated *in situ* by the thermolysis or photolysis of α-diazo-carbonyl compounds in the presence of aldehydes[56] or quinones[67,68], only 1,4-cycloaddition products having the structure of oxodioxans are isolated:



It is noteworthy that such a comparison of the reactivity of ketens generated *in situ* by two different methods in the presence of aldehydes is not entirely valid, since in the examples quoted the ketens, whose formation was suggested, have different structures; furthermore carbonyl compounds with insufficiently polarised carbonyl groups were employed as intercepting agents in these investigations[56,67,68]. This probably in fact accounts for the preferential 1,4-cycloaddition rather than 1,2-cycloaddition.

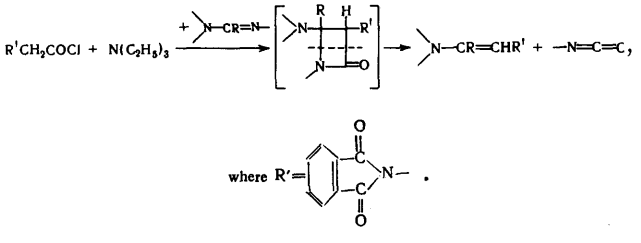
d. Cycloaddition to the N=N Bond

The cycloaddition of stable ketens, for example diphenylketen, to azo-compounds is achieved only on ultraviolet irradiation with formation of 1 : 1 adducts having the structure of 1,2-diazacyclobutan-3-one[69,70]. In contrast, the reaction of azo-compounds with the intermediate diphenylketen generated *in situ* by the photolysis of α-diazocarbonyl compounds leads to both 1 : 1 [71] and 2 : 1 [68] adducts:

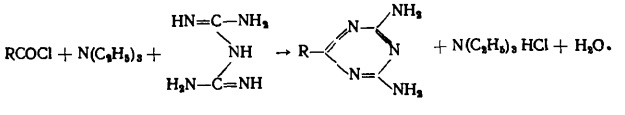


e. Cycloaddition to Amidines, Guanidines, and Urea Derivatives

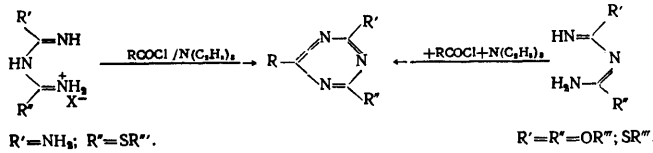
The addition *in situ* of intermediate ketens to amidines fully substituted at the nitrogen atom probably takes place at the C=N bond with formation of β-lactams[72]; the authors believe that further degradation of the lactams in fact results in the formation of the final products—an enamine and an isocyanate; in this case the reaction of the chloride of phthaloylglycine with triethylamine was employed to generate the keten; in the presence of azomethines, the reaction[51-54] (see preceding page) led to the formation of β-lactams in high yields:



When acid chlorides react with diguanidine in the presence of triethylamine, derivatives of 1,3,5-triazine are formed[73,74]:



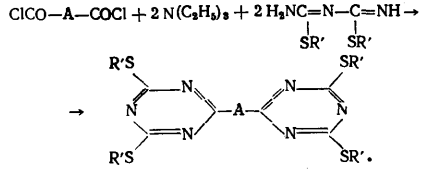
The corresponding 1,3,5-triazines are produced also when derivatives of biuret and dithiobiuret and *S*-alkylguanylisothiuronium salts are used as the intercepting agents[75]:



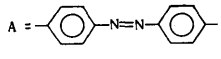
However, it should be noted that not only the chlorides of mono- and di-substituted acetic acids, in which a hydrogen atom is retained in the α-position, but also the halides

of acids lacking the capacity to serve as a source of intermediate ketens, for example trichloroacetyl chloride, substituted benzoyl chlorides, and the chlorides of $\alpha\beta$-unsaturated acids, were used in these reactions. These findings suggest that the synthesis of trazines under conditions of this kind may not in fact be accompanied by the formation of ketens as intermediate structures.

The interaction of dicarboxylic acid chlorides with triethylamine in the presence of dithiobiuret derivatives leads to the formation of the corresponding bistriazines [75]:

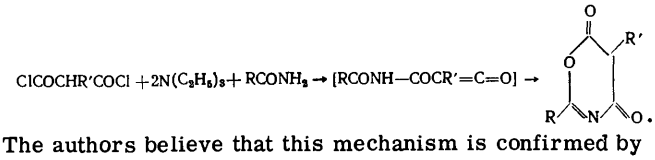


When A = $(CH_2)_n$, this process may be accompanied by the intermediate formation of a keten or a bisketen, while with

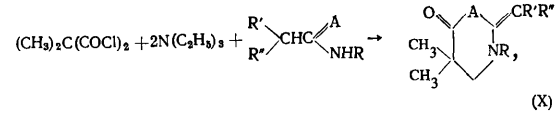


intermediate ketens are not formed.

Ziegler and coworkers [76,77] proposed a "keten" mechanism for the synthesis of dioxo-1,3-oxazines by the interaction of unsubstituted or monosubstituted malonic acid chlorides with amides in the presence of triethylamines:

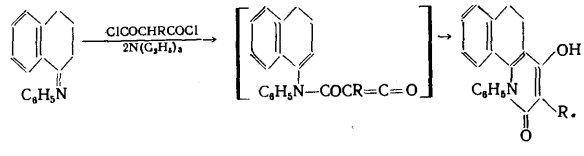


The authors believe that this mechanism is confirmed by the fact that they were unable to achieve analogous reactions with disubstituted malonyl dichlorides. However, some time later Martin et al. [78] synthesised successfully a number of derivatives of 1,3-oxazine, 1,3-thiazine, and pyrimidine (X) by the interaction of disubstituted malonyl dichlorides with amides, thioamides, and amidines in the presence of triethylamine:

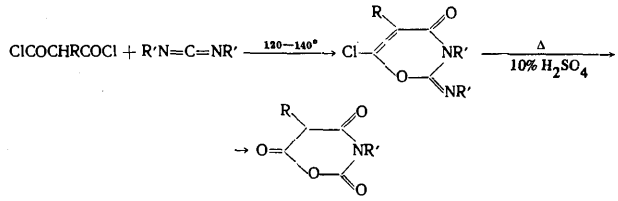


(X)

where A = O, S, or NR'''. Of course in this case the intermediate formation of a keten cannot occur. Furthermore in the reaction of butyramide with dimethylmalonyl dichloride the derivative of dioxo-1,3-oxazine (X, A = O, R' = R'' = CH_3, are obtained both in the presence [in this case R = $COCH(CH_3)_2$] and in the absence (R = H) of triethylamine. However, the formation of ketens in the reaction of monosubstituted malonyl dichlorides with tertiary amines is confirmed not only by the formation of 2-pyridones when ketimines and azomethines are employed as "interceptors" but also by infrared spectroscopic data [79-81]:



It is suggested [82] that the synthesis of barbituric acids by the cycloaddition of monosubstituted malonyl dichlorides to carbodi-imides also takes place by a "keten" mechanism:



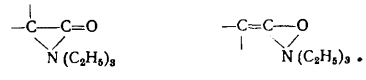
where R = H or alkyl and R' = H or C_6H_5.

4. CYCLIC DI- AND TRI-MERISATION

Reactions involving cycloaddition to ketens *in situ* are complicated by their polymerisation, which is usually limited to di- and tri-merisation. These side processes are most significant in the generation of ketones from acid chlorides under the action of trialkylamines.

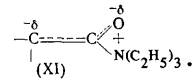
Even in the early studies by Staudinger [83,84] it was noted that stable ketens polymerise in the presence of tertiary amines. It would appear that this must be an indication of the interaction of ketens with trialkylamines, but there is still not single view concerning the nature of this interaction.

Wedekind [85,86] isolated in low yields weakly basic compounds which, according to their composition, appeared to be the products of the addition of triethylamine to keten in proportion of 1 : 1 ("ketenium" compounds) or 2 : 1 ("ketenates"). The following mesomeric structures with pentavalent nitrogen were attributed to the "ketenium" compounds:



Wedekind's results were not examined further for almost 30 years until Miller and Johnson [87] disproved the existence of the "Wedekind ketenium bases", having shown that the "ketenium" compounds are in fact the diethylamides of the corresponding acids, formed as a result of the presence of an admixture of diethylamine in the initial triethylamine. This accounts for both the low yield of Wedekind's "ketenium" compounds and their "anomalous" (according to Wedekind) reactivity.

Pracejus and Oehme [88] were unable to detect by infrared spectroscopy the interaction of trialkylamines with ketens and the possible structure of the adduct (XI) presented below was rejected on the basis of spectroscopic data:



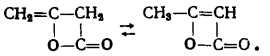
(XI)

However, subsequent kinetic investigation and the measurement of the isotope effect in the alcoholysis of ketens in the presence of tertiary amines enabled Tille and Pracejus [89] to attribute the structure (XI) to the postulated keten–amine complex.

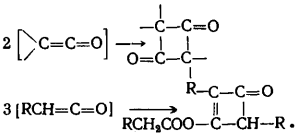
Di- and tri-merisation of ketens *in situ* is observed in all the methods of their formation without exception [2,3,5,90-92]. The catalysis of these processes by tertiary amines and their salts was investigated in greatest detail [93]. The study of the polymerisation of ketens *in situ* and the dependence of the structure of the keten dimers and trimers on the method of their formation permits controlled synthesis of products with a specified degree of polymerisation [94].

The dimer of the simplest keten (diketen) is obtained in high yield from keten *in situ* in the interaction between acetyl chloride and trialkylamines[93]. It is noteworthy that the rate of dimerisation of keten *in situ* is higher than the rate of dimerisation of the stable keten.

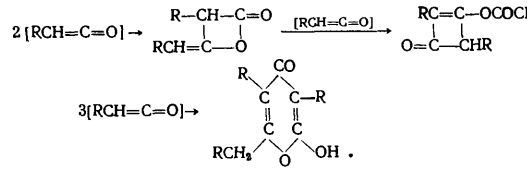
With the aid of modern methods for the investigation of structures (nuclear magnetic resonance[95], isotope methods[96]), it was possible to resolve the long-standing controversy concerning the structure of diketen and to demonstrate that it is a β-lactone:



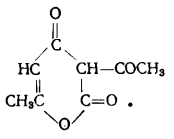
Later it was established[94] that, with the exception of keten itself, which is readily converted into the β-lactone even in the absence of catalysts, other ketens dimerise spontaneously *in situ* to cyclobutane-1,3-diones[95] or trimerise with formation of 3-hydroxycyclobutenone derivatives[97]:



Tertiary amines and their salts catalyse both the dimerisation *in situ* of the intermediate aldoketens, formed in the reaction between acid chlorides and tertiary amines, to β-lactones[98] and their trimerisation to 3-acylhydroxybutenones[99] (with R = alkyl) or pyranones (with R = aryl)[100]:



In addition in the case of an unsubstituted keten formed *in situ* in the interaction between acetyl chloride and triethylamine there is a possibility of further dimerisation of the diketen with formation of a tetramer—dehydroacetic acid (XII)[101]:

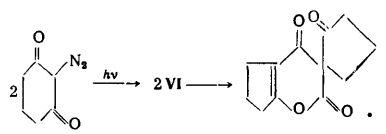


(XII)

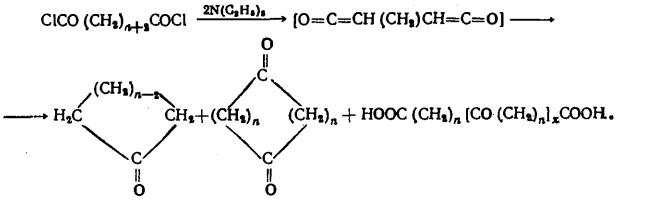
Ketens formed in the dehalogenation of α-halogeno-acid halides with zinc dimerise *in situ* in a different way. Here, the zinc halide formed in the reaction favours the dimerisation of the ketens to β-lactones with both R = alkyl and R = aryl[95].

Ketens derived from α-diazo-carbonyl compounds dimerise *in situ* in the presence of silver and copper catalysts for the Wolff rearrangement with formation of cyclobutane-1,3-diones[68].

Stetter and Kiehs[102] showed that the dimer of the intermediate keten derived from 2-diazodihydroresorcinol is a spiropyranone:



Acid dichlorides of the type $ClCO-(CH_2)_nCOCl$ react with tertiary amines in an unusual way. The intermediate bisketens formed in this case are converted into a mixture of cyclic ketone and diketone; furthermore, the formation of a polymer was observed[17-21] but its structure was not established:



Certain biologically active natural compounds previously difficult to obtain were synthesised by this method (muscone, civetone, and others). The concentration of the reactants plays a decisive role in this synthesis: for example, with sebacyl dichloride cycloketones can be isolated only when the reaction is carried out in highly dilute ethereal solutions.

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Phosphorus Hydrides

I.M.Osadchenko and A.P.Tomilov

The chemistry of phosphorus hydrides has assumed considerable importance—phosphine is the starting material for the synthesis of numerous organophosphorus compounds and fire resistant polymers; in recent years phosphorus hydrides have begun to be used in the semiconductor industry for the preparation of metal phosphides with a high degree of purity. The range of applications of phosphorus hydrides has increased in connection with the synthesis of a new class of complex compounds.

The review deals with the physical and chemical properties of the phosphorus hydrides investigated. The methods of synthesis of phosphorus hydrides, particularly phosphine, are examined. The applications of phosphine in industry are discussed. The bibliography comprises 141 references.

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Phosphorus forms the following compounds with hydrogen: PH_3—gaseous hydrogen phosphide (phosphine)[1]; P_2H_4—liquid hydrogen phosphide (diphosphine, biphosphine[1], hydrogen hemiphosphide), and solid hydrogen phosphides [1-5] which include compounds with the empirical formulae $P_{12}H_6$, P_7H_2, P_9H_2, and $(PH)_x$. There is no doubt about the structural formulae of the first two compounds, but no single view exists concerning the structure of the solid hydrides.

1. HYDROGEN PHOSPHIDE (PHOSPHINE)

a. Physical Properties

Phosphine is a colourless gas with an unpleasant smell, sparingly soluble in water (26 volumes of the gas in 100 volumes of water) and readily soluble in carbon disulphide, benzene, cyclohexanol, ether, and other solvents [1-3]. Some of the physical properties of phosphine [2,3] are listed in Table 1. Phosphine has been investigated by infrared, microwave, NMR, and Raman spectroscopy and mass spectrometry [2].

The structure of the phosphine molecule has been established on the basis of infrared and microwave spectra[2]. The molecule has the form of a trigonal pyramid with the phosphorus atom at the apex and has low polarity (dipole moment 0.55 D). All three hydrogen atoms in the molecule are equivalent, with the P–H distance 1.419 Å the height of the pyramid 0.70 Å, and the H–P–H angle 93.7°. [2,3]

The density and compressibility of phosphine have been thoroughly investigated to determine the atomic weight of phosphorus. These data have established that the molecular weight of phosphine is 34.000. Accurate determinations of the density and the compressibility made it possible to establish the deviation of phosphine from ideal gas laws and to derive an equation of state for phosphine vapour [2]. The physical constants of liquid phosphine show [2] that there is some molecular association in the liquid state but that the degree of association is much less than in water.

Comparison with the hydrides of the adjacent elements in the Periodic Table shows that phosphine forms few hydrogen bonds or none at all.

The surface tension of phosphine at −100°C is [2] 22 dyn cm^{-1}. In the solid state phosphine exists in four modifications with transition temperatures of −185.06°, −223.75°, and −242.87°C. Over a short temperature range near the absolute zero the supercooled form has an anomalously high heat capacity. The solution of phosphine in liquid ammonia conducts electricity. When the solution is electrolysed, elemental phosphorus is deposited at the anode[4,5]. Evidently ammonia forms a salt-like compound with phosphine having the probable formula $NH_4^+(PH_2)^-$.

Table 1. Physical properties of phosphine (PH_3).

B.p., °C	Q_{vap}, kcal mole^{-1}	Trouton's constant	ρ, g cm^{-3}	M.p., °C	Q_f, kcal mole^{-1}	$t_{crit.}$, °C	$P_{crit.}$, atm	Q_{form}, kcal mole^{-1}
−87.8	3.49	18.8	1.529	−133.8	0.27	+51	64	+2.29

Phosphine is extremely poisonous and must be handled with care—it is a poison which acts predominantly on the nervous system and interferes with metabolism. The maximum permissible concentration of phosphine in industrial buildings amounts to [6] 0.1 mg m^{-3}.

b. Chemical Properties

When phosphine is heated in the absence of air, it dissociates:

$$4\,PH_{3(gas)} \rightleftarrows P_{4(gas)} + 6H_{2(gas)}.$$

The thermal dissociation of phosphine was investigated in detail by Ipat'ev [7-9] and Frost [10]. At a high temperature the equilibrium is displaced to the right but at low temperatures the gas is quite stable.

The reaction of phosphine with oxygen is a branched-chain process resembling the oxidation of white phosphorus [2,11,12]. Studies on the mechanism of the combustion of phosphine were begun by van de Stadt [12] and the problem was elucidated in detail by Semenov [11].

In air phosphine burns with formation of phosphorus pentoxide:

$$2PH_3 + 4O_2 \rightarrow P_2O_5 + 3H_2O.$$

On considerable rarefaction and particularly in the presence of water vapour, slow oxidation without inflammation, accompanied by the formation of phosphorus acids, may take place [13]:

$$2PH_3 + 3O_2 \rightarrow 2H_3PO_3,$$
$$PH_3 + O_2 \rightarrow HPO_2 + H_2.$$

It has been suggested [14] that the first stage of the slow oxidation is the formation of phosphine oxide PH_3O. However, the latter could not be obtained by direct oxidation of phosphine with nitrobenzene or trimethylamine oxide [10]. The attempt to synthesise phosphine oxide by reducing phosphorus oxychloride and oxybromide with metal hydrides (LiH, $LiBH_4$) in ether at low temperatures was unsuccessful; phosphine oxide was not isolated probably because of its high reactivity, the tendency to polymerise with the elimination of water, and thermal instability at temperatures in excess of $-115°C$.

Since it is a branched chain reaction, the oxidation of phosphine has upper and lower critical pressure limits. Inert gases decrease the lower limit, preventing diffusion to the walls of the vessel, if the pressure of the inert gas is less than that of phosphine or oxygen. Irradiation with ultraviolet light reduces the limiting oxygen pressure [2] through phosphines' forming a substance (possibly atomic hydrogen) which affects the chain reaction. The upper limiting pressure of oxygen in the oxidation of phosphine is independent of the dimensions of the reaction vessel, decreasing somewhat in the presence of an inert gas.

The solution of phosphine in water has virtually no acid or basic properties; however, phosphine hydrate probably does exist. Phosphine dissolved in water gradually decomposes into hydrogen, phosphorus, and a solid phosphorus hydride.

With acids, phosphine forms phosphonium salts. Phosphonium halides can be obtained by the reaction of phosphine with hydrogen halides and the sulphate and perchlorate by the reaction with sulphuric and perchloric acid. The reaction with hydriodic acid can be represented by the equation

$$PH_3 + HI \rightarrow PH_4I.$$

In water these compounds hydrolyse almost completely with formation of phosphine, the hydrogen ion, and the halide ion.

Phosphine is a more powerful reducing agent than ammonia; it reacts spontaneously with chlorine at room temperature, forming phosphorus chlorides and hydrogen chloride, and with fused sulphur it forms hydrogen sulphide. Hydrogen sulphide and phosphine also interact (much more slowly than phosphine and sulphur), hydrogen and phosphorus sulphides being formed [2]. Reaction between phosphine and phosphorus trihalides leads to the formation (together with other products) of elemental phosphorus and the hydrogen halide:

$$PCl_3 + PH_3 \rightarrow 2P + 3HCl.$$

The reaction with pentahalides yields the trihalide and the hydrogen halide:

$$3PCl_5 + PH_3 \rightarrow 4PCl_3 + 3HCl.$$

As a reducing agent, phosphine reacts with many oxidising agents [2]: for example, it reduces metal ions to the free metal:

$$PH_3 + 6AgNO_3 + 3H_2O \rightarrow 6Ag + 6HNO_3 + H_3PO_3,$$

oxides to the phosphides [15]:

$$In_2O_3 + 2PH_3 \rightarrow 2InP + 3H_2O,$$

and iodine to iodides [2]:

$$PH_3 + 3I_2 + 3H_2O \rightarrow H_3PO_3 + 6HI.$$

The reactions of phosphine with silver nitrate, iodine, potassium permanganate, etc. are used for its quantitative determination. The phosphine molecule has a free electron pair at the phosphorus atom and exhibits electron-donor properties, so that phosphine, like ammonia, shows at least some tendency to form complexes with electron-acceptor molecules. For example, phosphine forms complexes of the type $P_2Hg_3.3HgCl_2$ with mercuric chloride [2], $PH_3.BF_3$ and $PH_3.2BF_3$ with boron trifluoride, $2PH_3.B_2H_6$ with diborane, and $[V(CO)_4PH_2]_2$ with vanadium hexacarbonyl [16].

Phosphine reacts with many organic compounds and this leads to the possibility of synthesising compounds with a phosphorus–carbon bond which cannot be prepared in other ways.

The interaction of phosphine with organic compounds takes place stepwise with formation of mono-, di-, and trisubstituted phosphines and sometimes quaternary phosphonium compounds in the presence of strong inorganic acids. The reaction of phosphine with aldehydes and ketones has been thoroughly investigated [17–18]. In the presence of a strong acid this reaction takes place according to the following general equation:

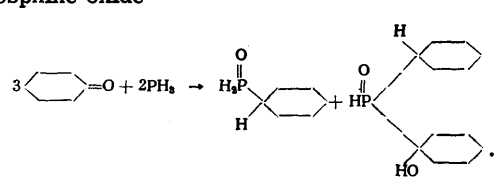
$$PH_3 \xrightarrow{>C=O} >C(OH)-PH_2 \xrightarrow{>C=O} (>C-OH)_2PH \xrightarrow{>C=O}$$

$$(>C-OH)_3P \xrightarrow{>C=O,HX} (>C-OH)_4PX.$$

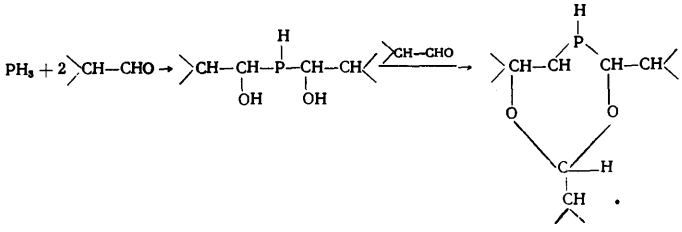
With aliphatic aldehydes, a mixture of mono-, di-, and tri-substituted phosphines and quaternary phosphonium salts is obtained, while aliphatic ketones and aromatic aldehydes yield mono-, and di-substituted phosphines [19,20], which isomerise to phosphine oxides. A classical example of the reaction of phosphine with aldehydes is the reaction of phosphine with formaldehyde in aqueous solution in the presence of hydrochloric acid discovered by Hofmann [23]. The reaction yields tetra(hydroxymethyl)phosphonium chloride—the starting material for the synthesis of many compounds, including fire-resistant polymers [24,25]. Soborovskii and coworkers [26,27] later showed that the reaction of phosphine with formaldehyde can take place also in the absence of a catalyst under a pressure of 150–300 mmHg. Under pressure paraformaldehyde reacts with phosphine [26,27] forming tri(hydroxymethyl)phosphine. With acetone, isopropoxyisopropylphosphine is obtained:

$$2CH_3COCH_3 + PH_3 \rightarrow (CH_3)_2CH-\overset{O}{\overset{\|}{P}}-C(OH)(CH_3)_2$$

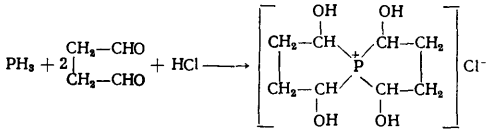
while the reaction with cyclohexane gives a mixture of cyclohexylphosphine oxide and cyclohexyl-1-hydroxycyclohexylphosphine oxide [19,20]



The condensation of phosphine with α-substituted aldehydes stops at the stage involving the formation of a disubstituted product[21], which is converted in the presence of an excess of the aldehyde into a heterocyclic compound:



Phosphine reacts with dialdehydes, forming a spiro-ring compound[19,20]:



but the rings are only five- and six-membered; glyoxal gives rise to a product with a linear structure; the reaction with epoxy-compounds gives low yields of a mixture of mono-, di-, and tri-substituted phosphines; for example, the reaction with epoxyethane takes place as follows[21,24,28]:

$$PH_3 + 6CH_2{-}CH_2 \rightarrow HOCH_2CH_2PH_2 + (HOCH_2CH_2)_2PH + (HOCH_2CH_2)_3P .$$

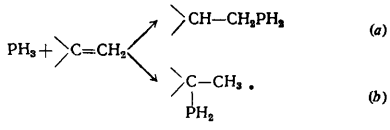
With organomagnesium compounds phosphine forms monosubstituted analogues of the Grignard reagent[21] with high reactivity:

$$PH_3 + RMgX \rightarrow H_2PMgX + RH .$$

Phosphine adds to olefinic compounds in the presence of strong acids[29,31] with formation of mono-, di-, and trisubstituted phosphines and phosphonium salts and also to 1-olefins[32] in the presence of catalysts at 100°C:

$$PH_3 + CH_2{=}CH{-}CH_2Cl \rightarrow H_2PCH_2CH_2CH_2Cl .$$

In a radical mechanism the phosphorus atom adds to the terminal carbon atom (*a*) and in an ionic mechanism to the middle carbon atom (*b*):



With tetrafluoroethylene, a mixture of products is formed[31]:

$$4CF_2{=}CF_2 + 4PH_3 \rightarrow F_2CH{-}CF_2PH_2 + H_2P{-}CF_2{-}CF_2{-}PH_2 + (F_2CH{-}CF_2)_2PH .$$

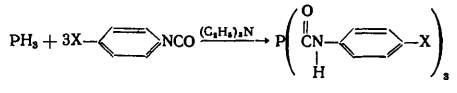
Phosphine reacts with organic acid chlorides to form a mixture of mono-, di-, and tri-substituted products[31]:

$$CCl_3COCl + PH_3 \rightarrow CCl_3COPH_2 + HCl .$$

The reaction with alkyl halides takes place similarly[21]:

$$PH_3 + RX \rightarrow RPH_2 + HX ,$$

while the reaction with isocyanates is



where X = H, Cl, or NO_2.

2. DIPHOSPHINE

Diphosphine is a colourless highly refractive liquid, which ignites spontaneously in air at room temperature (the principal physical properties are listed in Table 2) and is insoluble in water; alcohol and turpentine appear to dissolve diphosphine (P_2H_4), but the solution is very unstable and rapidly decomposes in the presence of the catalysts: hydrogen chloride, charcoal, pumice[2]. Diphosphine is sparingly soluble in liquid ammonia, and the solutions are unstable and readily decompose. Evers and Street[33,34] stated that diphosphine decomposes on storage into phosphine and solid phosphorus hydrides of composition P_9H_2 and P_5H_2, which decompose further to elemental phosphorus. When diphosphine is stored above 0°C or in the presence of hydrochloric acid, it gradually turns yellow owing to the precipitation of solid phosphorus hydrides†. The structure of the diphosphine molecule was established by NMR:[35]

Table 2. Physical properties of diphosphine (P_2H_4).

B.p., °C	Q_{vap}, kcal mole^{-1}	Trouton's constant	ρ, g cm^{-3}	M.p., °C
56	6.89	21	(1.02—1.007)	—99

Diphosphine is a powerful reducing agent, largely resembling hydrazine in its chemical properties. Its reactions have been scarcely investigated. Gattermann and Hausknecht[36] unsuccessfully attempted to obtain compounds of diphosphine with aldehydes and ketones. Diphosphine was obtained in a mixture with phosphine for the first time in 1945 by Thenard[37,38], who allowed calcium phosphide to react with water:

$$Ca_3P_2 + 6H_2O \rightarrow 3\,Ca(OH)_2 + P_2H_4 + H_2 .$$

The possibility of synthesising diphosphine by this method was suggested long ago by Leverriers[39,40]. Subsequently this reaction was the sole preparative method for synthesising diphosphine[36,41]. According to the recommendations of Gattermann and Hausknecht[36], diphosphine is synthesised as follows.. The apparatus consists of a round-bottomed flask connected to a receiver via a cooling coil. The receiver is immersed in a cooling mixture. Water is poured into the flask and the apparatus is thoroughly flushed with hydrogen. The water is heated to 60°C and calcium phosphide is added in pea-sized lumps at 150–200 g h^{-1}. Diphosphine begins to collect in the cooled receiver after approximately 15 minutes.

Recently, reports have been published[42-44] on the preparation of liquid triphosphine (P_3H_5) by the decomposition of phosphine in a reactor consisting of two concentric tubes, the temperature of the inner tube being 65°, and that of the outer 63°C, and on its preparation by the hydrolysis of calcium and magnesium phosphides in the presence of arsenides and germanides with heating under a high pressure[42,43].

P_3H_5 was identified by mass-spectroscopy and gas-chromatography (on kieselguhr with silicone oil).

†Recently a new phosphorus hydride P_2H_2 was prepared by the pyrolysis of diphosphine[140].

3. SOLID PHOSPHORUS HYDRIDES

The most familiar solid phosphorus hydride, $P_{12}H_6$, is a pale yellow powder stable in air, insoluble in water and organic solvents, and soluble in diphosphine and fused yellow phosphorus. Its density, determined for a suspension in a mixture of chloroform and bromoform, is 1.83 g cm^{-3} at 19°C.[2] The product decomposes rapidly in the light, ignites spontaneously at 200°C, and vaporises without change only in a high vacuum.

The solid hydride $P_{12}H_6$ was obtained for the first time in 1827 by Rose[45,46]. When diphosphine was passed through an aqueous solution of hydrochloric acid, Rose observed the precipitation of a solid yellow compound. Later this method was employed by Thenard[37,38] and Schenk[47]. Schenk prepared $P_{12}H_6$ by the reaction of calcium phosphide with water followed by treatment of the gas evolved with hydrochloric acid. The yield of the solid hydride was very low—about 3 g per kilogramme of calcium phosphide. Gattermann[36] improved somewhat the experimental technique but even in his synthesis the yield of $P_{12}H_6$ does not exceed 8 g per kilogramme of calcium phosphide. Up to the present time, this is the only method suitable for preparative purposes.

Other methods of synthesising the solid phosphorus hydride have been reported. Jolibois[48] stated that the solid hydride $P_{12}H_6$ may be obtained by the decomposition of zinc phosphide with hydrochloric acid. Later it was suggested that the hydride be obtained by the decomposition of aluminium phosphide with dry hydrogen chloride[2] or by the reaction of white phosphorus with potassium hydroxide in glycerol[49,50]. Rüdorf[51] suggested a synthesis of $P_{12}H_6$ from phosphorus iodide and water, in which the product is obtained in a low yield, and Besson[52] and Stock[53] proposed syntheses in which phosphine is passed through phosphorus trichloride or tribromide, but the method failed in practice.

Stock et al.[54] reported that the yellow phosphorus hydride $P_{12}H_6$ eliminates PH_3 on heating and is converted into the orange-red solid hydride P_9H_2. The same substance is obtained when liquid ammonia is allowed to react with $P_{12}H_6$,[33,54] the reaction being accompanied by the evolution of phosphine.

Hackspiel[55] showed that the solid hydride to which Thenard assigned the formula $P_{12}H_6$ in fact has the formula P_5H_2. This compound has acid properties and can form metal phosphides. In a vacuum P_5H_2 evolves pure phosphine.

Recently Weiberg and Müller-Schiedmayer[56] reported the preparation of a new phosphorus hydride with the formula $(PH)_x$ by the reduction of phosphorus halides and oxyhalides with lithium and aluminium hydrides in ethereal solution at low temperatures. The yield of this hydride can reach 90% in the reduction of phosphorus dibromide with lithium hydride at 30°C. It is a brown solid stable at room temperature. On heating to 400°C in a vacuum, it decomposes:

$$3(PH)_x \rightarrow 2xP + xPH_3.$$

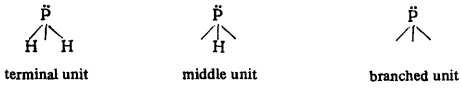
It exhibits weak basic properties, similar to those of trimethylamine, and is a powerful reducing agent—for example, on heating it reduces sulphuric acid to hydrogen sulphide. It is oxidised to phosphoric acid by strong oxidising agents such as hydrogen peroxide or sodium hypochlorite.

When yellow phosphorus is reduced electrochemically at a lead cathode[57], vigorous absorption of hydrogen without evolution of gaseous phosphorus-containing products is observed during the initial period. It is suggested[57] that the first stage of the reduction is the formation of the hypothetical hydride P_4H_4 by the reaction

$$P_4 \xrightarrow{4H^+,4e^-} P_4H_4.$$

This conclusion is based on the study of the variation of the concentration of yellow phosphorus during the electrolysis, but the hydride of the above composition was not isolated.

There exist various views concerning the structures of solid phosphorus hydrides. Royen[42,43] suggested that solid phosphorus hydrides are products of the sorption of PH_3 by one of the forms of yellow phosphorus. According to another view, solid phosphorus hydrides are macromolecular substances resembling in many respects organic plastics and phosphate glasses, which have the general formula P_nH_{n+2} and consist of three of the structural units shown below.



Diphosphine consists of two terminal units linked together. Triphosphone P_3H_5 consists of one middle and two terminal units. The hydride $(PH)_x$ consists only of middle units. There is probably a state of equilibrium between the groups, for example:

$$2\,\rangle PH \rightleftarrows -PH_2 + \rangle P.$$

The hydrides in which the molar H/P ratio is less than unity must contain branched elements in their structure; these compounds are probably analogous to three-dimensional polymers and this is why they cannot be dissolved in any solvent without breakdown of the molecule.

4. APPLICATIONS OF PHOSPHORUS HYDRIDES

Of the known phosphorus hydrides, only phosphine has practical importance. So far no applications have been found for the other hydrides. The possibility of the spontaneous ignition of phosphine constitutes a great risk in experiments with this material. For this reason, much attention has been devoted to the problem of the spontaneous ignition and stabilisation of phosphine. The spontaneous ignition temperature of pure phosphine in the presence of air is 140°C,[1] but when the gas contains a very small admixture of diphosphine (1 : 500), it ignites spontaneously in air even at −40°C.[1,2] The problem of the spontaneous ignition of phosphine has attracted attention for a long time. Ter-Gazaryan[58] believed that the most effective method for the purification of the gas from traces of other phosphorus hydrides and hydrogen is repeated liquefaction and fractional distillation of the liquid. However, later studies showed that the capacity of phosphine for spontaneous ignition can be suppressed by simpler means. Trautz[59] showed that the gas mixed with hydrogen and alcohol vapour does not ignite spontaneously. Graham[60,61], who studied the conversion from the inflammable to the non-inflammable form of the gas, established that, to achieve this conversion, it is sufficient to keep the gas under water containing air. The conversion can be achieved with the aid of a cork stopper or a lump of gypsum containing air in its pores. If the walls of the vessel are wetted with concentrated phosphoric, sulphuric, and arsenic acids, the conversion takes 2–3 min. Mercurous oxide acts most rapidly, while potassium hydroxide requires several hours for this purpose. Metallic potassium and its amalgam (one part of potassium in 350 000

parts of mercury) suppress the inflammability in several minutes. Johnson[62] recommends that alumina dehydrated at a low temperature be used as the drying agent for the preparation of non-inflammable phosphine. Thenard[37,38] and Amato[63] showed that phosphine loses the capacity for spontaneous ignition in air if it is treated with concentrated hydrochloric acid or stored in a glass vessel in sunlight. Under these conditions the diphosphine in the gas decomposes. Dilution of phosphine with an inert gas can also be used[64].

Until recently phosphine had only limited applications. Thus it was used to combat plant pests[65] and rodents[66], for the preparation of a layer of phosphides of metals resistant to mechanical, thermal, and chemical action, for the preparation of rare-metal phosphides used in semiconductor engineering, and for the preparation of phosphide bronzes used in machine engineering[66]. At present phosphine is attracting much attention in connection with possible new applications. For example, it has been found that phosphorus obtained by the thermal decomposition of its hydrides[67] has high purity and may be used as a semiconductor. The possibility of its military applications has also been noted[67a].

There exist wide possibilities for the application of phosphine in the synthesis of organophosphorus compounds, in particular the preparation of tetra(hydroxymethyl)phosphonium chloride—an intermediate in the manufacture of fire-resistant polymers[22,24,25], the preparation of extracting agents for rare metals, plasticisers for plastics[19,20], etc.

5. METHODS OF PREPARATION OF PHOSPHINE

Since there is a much greater variety of data on phosphine compared with the other hydrides, the methods of its preparation are discussed separately.

a. Synthesis from Metal Phosphides

Phosphine can be obtained by the action of water or dilute acid on alkali and alkaline earth metal phosphides. For example, Hugot[68] obtained phosphine by the action of water or dilute acids on sodium trihydrophosphide:

$$Na_3H_3P_2 + 3H_2O \rightarrow 2PH_3 + 3NaOH,$$

or

$$Na_3H_3P_2 + 3HCl \rightarrow 2PH_3 + 3NaCl,$$

or by heating this substance to 100°C at a reduced pressure. As the temperature is increased, more hydrogen and less phosphine is obtained.

A number of workers recommend that phosphine be obtained by the action of water or a dilute acid on calcium phosphide[35-38,69]. Moissan[70] was the first to obtain phosphine from calcium phosphide and water:

$$Ca_3P_2 + 6H_2O \rightarrow 2PH_3 + 3Ca(OH)_2.$$

As already mentioned, diphosphine is obtained as a side product in this process.

The gas produced by the action of water on technical calcium phosphide contains considerable amounts (up to 30%) of diphosphine and hydrogen. Phosphine can be synthesised by the action of water and hydrochloric acid on a specially prepared mixture of calcium and aluminium phosphides and on the phosphides of iron, magnesium, and aluminium[71].

The reaction of aluminium phosphide[49,50] with water takes place with evolution of much heat and is difficult to control. Kuznetsov and coworkers[72,73] showed that phosphine can be synthesised by the decomposition of water on aluminium phosphide suspended in an inert liquid; it is stated that the decomposition of aluminium phosphide suspended in organic solvents (methanol, ethanol, acetone, etc.) takes place comparatively smoothly and is easier to control. The decomposition of zinc phosphide with dilute acids (hydrochloric and sulphuric acids) has been thoroughly studied:

$$Zn_3P_2 + 6HCl \rightarrow 2PH_3 + 3ZnCl_2.$$

This reaction is most often used for the synthesis of phosphine[3]. The methods of preparation of phosphine discussed above have certain disadvantages[74-78]: contamination of the gas, expense, and the formation of waste—spent solutions and sludge.

b. Synthesis from Other Phosphorus Compounds

Hofmann[41] attempted to prepare pure phosphine by the decomposition of phosphonium iodide with water or potassium hydroxide solution, but it was found that the resulting gas contains also diphosphine and may ignite spontaneously in air:

$$PH_4I + KOH \rightarrow PH_3 + KI + H_2O.$$

Berzelius and Lüpke[79-81] obtained gaseous phosphine by the reduction of phosphites or a mixture of phosphite and hypophosphite with iron or zinc. An American patent[82] states that, when phosphites and hypophosphites are heated to 300–400°C, phosphine is obtained in yields of 18 and 46% respectively. Thorpe and Tutton[83] obtained phosphine by the action of dilute hydrochloric acid on the amide of phosphorous acid.

Phosphine can be synthesised by heating lower oxygen-containing phosphorus acids, for example hypophosphorous and phosphorous acids[45,46]:

$$2H_3PO_2 \rightarrow PH_3 + H_3PO_4,$$
$$4H_3PO_3 \rightarrow PH_3 + 3H_3PO_4,$$

but in this reaction only 50 and 25% of phosphorus respectively is usefully employed. It has been reported that phosphine is obtained when atomic hydrogen is allowed to react with lower phosphorus acids[84], the reactions including cathodic reduction[85], thermal decomposition of lower phosphorus hydrides[86], particularly at a reduced pressure, for example:

$$15P_2H_4 \rightarrow 18PH_3 + P_{12}H_6,$$
$$P_{12}H_6 \rightarrow 2PH_3 + 10P,$$

and also in acid and alkaline hydrolysis of phosphorus sulphides (yield 3–5%).[2]

Gutmann[87] reported that, when phosphorus halides are reduced with hydrogen in the gas phase in a gas-discharge tube, phosphine is formed together with red phosphorus.

Paddock, Wiberg, and Müller-Schiedmanyer[14,56,88,89] investigated the hydrogenation of phosphorus halides and oxyhalides with metal hydrides in ethyl ether. They showed that, together with phosphine, the reaction products may contain the solid hydride to which the formula $(PH)_x$ was attributed:

$$PX_3 \xrightarrow[-3X^-]{+3H^+} \begin{cases} PH_3 & \text{(a)} \\ (PH)_x + H_2 & \text{(b)} \end{cases}.$$

By choosing appropriate conditions, the reaction can be driven along pathway (a) or (b). In the synthesis of phosphine it is best to employ as low a temperature as possible. The maximum yield of phosphine (85%) was achieved in the reduction of phosphorus trichloride at −115°C with aluminium hydride and in the reduction of $POCl_3$ at −115°C with lithium tetrahydroaluminate.

The reduction of phosphorus pentahalides [88] with metal hydrides at temperatures between −80° and −100°C led to the formation of a equimolar mixture of phosphine and hydrogen. It has been noted [90] that phosphine (and other hydrides of Group V elements of the Periodic System) can be obtained by the reduction with lithium hydride of phosphorus halides at temperatures in the range 150–250°C. Lithium hydride is mixed with an inert powder (quartz, sodium chloride, etc.) in an inert gas, the halide vapour in an evaporator being supplied to the fluidised bed from below.

c. Synthesis from Elemental Phosphorus

Chemical methods. Phosphine may be obtained by the reaction of phosphorus with hydrogen, but only in a small yield. Rötgers [91] was the first to report the formation of phosphine by the reaction of incandescent red phosphorus with hydrogen. Dolique [92] did not confirm these data. He observed the formation of only traces of phosphine at 400°C. The use of decomposition and hydrogenation catalysts (activated charcoal, kieselguhr, pumice, nickel, copper, and iron) had no effect on the results.

Ipat'ev, Nikolaev, and Frost [7–10] observed the formation of phosphine on heating yellow phosphorus with hydrogen in a sealed tube at 360°C; the yield did not exceed 2%. Langmuir [93,94] obtained phosphine by the reaction of phosphorus with atomic hydrogen, formed from molecular hydrogen by heating the latter in the presence of platinum, palladium, or tungsten to 1100°C at a pressure of 0.001–0.2 mmHg. The synthesis of phosphine by the action on phosphorus of hydrogen activated in an electric discharge or by high-energy radiation has been patented [95].

A number of methods of the synthesis of phosphine are based on the reduction of yellow phosphorus with hydrogen at the instant of precipitation. The experiments of Vournasos [96] constituted one of the first studies based on this principle. By heating a mixture of sodium formate and red phosphorus, he obtained a spontaneously inflammable gas. Probably in this gas the hydrogen formed in the decomposition of formate reacted with the phosphorus:

$$6\,HCOONa \rightarrow 6\,H + 3Na_2C_2O_4,$$
$$2\,P + 6H \rightarrow 2PH_3.$$

Yellow phosphorus is reduced by the hydrogen evolved when zinc reacts with a concentrated solution of alkali. The reaction begins about 60°C. Brössler [97] obtained phosphine by adding yellow phosphorus to dilute sulphuric acid. Vitali [98] established that the presence of mercuric chloride in the acid retards the formation of phosphine.

Dusart [84] and Davy [99] believe that only traces of phosphine can be obtained by this procedure, while Dumas [100] altogether rejects the possibility of the formation of phosphine in this reaction. Oppenheim [101] obtained phosphine by heating red phosphorus with concentrated hydrochloric acid in a sealed tube to 600°C; when hydriodic acid is used, the same effect is achieved on heating to 160°C. Oppenheim heated phosphorus with glacial phosphoric acid in a sealed tube at 200°C, which led to the formation of hypophosphorous acid and this was subsequently converted into phosphine and phosphoric acid. Weyl [102] obtained phosphine by the action of hydrogen peroxide on red phosphorus. It has been stated [103] that phosphine is formed when ammonia and sodamide and also a mixture of sulphuric and phosphoric acids are allowed to react with yellow phosphorus.

Palmer [104–107] suggested that phosphine be obtained by the action of zinc and cadmium amalgams in acid solutions on yellow phosphorus. The yield of phosphine reaches 90%, but the apparatus and technology of the synthesis are very complex; furthermore, apparatus for the preparation of the amalgams is necessary.

In much later patents [108–110], it was stated that phosphine can be synthesised by heating white phosphorus with water vapour in the presence of phosphorus pentoxide:

$$8P + 12H_2O \rightarrow 3H_3PO_4 + 5PH_3.$$

The content of phosphine in the gas reaches 94–99 vol.% (yield 62.5%). Condensed phosphates are produced in addition to phosphine. For a successful reaction, it is recommended that finely ground red phosphorus containing up to 4% of white phosphorus be used. Because of the highly corrosive nature of the medium, the process is carried out in a graphite or quartz reactor. In the absence of phosphorus pentoxide the reaction of phosphorus with water is possible only under a pressure of 50 atm and in the presence of catalysts [111,112].

Phosphine is known to form [113] in small amounts in the industrial preparation of yellow phosphorus by the thermal reduction of phosphorites in electric furnaces as a result of the partial reduction of the elemental phosphorus. The phosphine content in the furnace gases amount to 1 vol.%.

Phosphine was obtained for the first time by Gengembre [114] in 1773 and independently by Kirwan [115] in 1789 by boiling a concentrated solution of potassium hydroxide with yellow phosphorus. Rose [45,46], who made a detailed study of this reaction, found that the gas is evolved at a temperature as low as 15°C. The phosphine obtained by this method contains a considerable amount of diphosphine. The main reaction may be represented by the equation

$$4P + 3KOH + 3H_2O \rightarrow 3KH_2PO_2 + PH_3,$$

and the side reaction by

$$6P + 4KOH + 4H_2O \rightarrow 4KH_2PO_2 + P_2H_4.$$

The diphosphine produced decomposes partially with formation of a solid phosphorus hydride:

$$15\,P_2H_4 \rightarrow P_{12}H_6 + 18PH_3.$$

A considerable amount of hydrogen is produced together with phosphine. According to the data of Dumas [99] [Davy ? or Dumas [100] ? (Ed. of Translation)] and Hofmann [41], it is difficult to obtain phosphine containing less than 55–60% of hydrogen. Hydrogen is formed by the reaction

$$4P + 5KOH + 3H_2O \rightarrow PH_3 + 2H_2 + KH_2PO_2 + 2K_2HPO_3.$$

When calcium hydroxide is used, the hydrogen content of the gas is 89–90%. It is stated in patents [116–118] that, when an alcoholic solution of alkali (more than 70% of alcohol) is used, 95% of the theoretical yield of phosphine is obtained.

Phosphorus is hydrogenated by the organism phihothion [119].

All the methods of preparation of phosphine from elemental phosphorus enumerated above give relatively low yields of the product with considerable amounts of impurities. The possibility of synthesising phosphine by the electrochemical reduction of yellow phosphorus must be regarded as more promising.

Electrochemical Synthesis

The preparation of phosphine with the aid of an electric current was first reported by Grove [120] in 1863. He passed an electric current through moist phosphorus in order to fuse it and observed the formation of phosphine.

Blumenberg [65] asserted that phosphine can be obtained like arsine by the cathodic reduction of phosphorus salts and oxides. However, this has still not been confirmed. Subsequently it was stated in a French patent [105] that, in the preparation of hypophosphorous acid by the anodic oxidation of yellow phosphorus (or phosphorus alloys—for example ferrphosphorus), phosphine is formed at the cathode, probably as a result of the reduction of hypophosphorous acid. This was also reported by Baudler [85], but the process conditions were not given. Somewhat later, West German, British, and United States patents appeared [74,121,122], in which it is suggested that phosphine be obtained by the cathodic reduction of yellow phosphorus in aqueous solutions of salts and acids on metals with a high hydrogen overvoltage, for example, lead, zinc, mercury, etc. Aqueous solutions of hydrochloric, sulphuric, phosphoric, and acetic acids and their salts were used as the catholyte. To prevent the oxidation of phosphorus and its reduction products, the cathodic compartment was separated from the anodic compartment by a diaphragm. Since the solubility of phosphorus in aqueous solutions is very low, the solution was stirred mechanically (or magnetically) to emulsify the phosphorus. Price and Gordon [74,121,122] assert that, under these conditions, fused phosphorus rises vertically along the cathode like liquid in a wick ("wick effect"), wetting its entire surface. Platinum, lead, lead dioxide, lead–arsenic alloy, graphite, and stainless steel have been used as anode materials. The maximum yield of phosphine was observed in a solution of orthophosphoric acid (4 M) at mercury and zinc cathodes and amounted to 87%.

It is stated in patents [121,122] that the yield of phosphine falls with time and, in order to improve the yield, it is recommended that salts of certain metals (lead, barium, calcium, zinc, etc.) be added to the catholyte. The temperature is kept above the melting point of phosphorus (44°C) and below the boiling point of the solution (below 110°C) and the current density is maintained in the range 150–400 A m^{-2}. The authors do not describe the optimum conditions.

Recently a large number of patents have been published [75-78,123-132], describing various versions of the electrochemical method for the preparation of phosphine and its further development. The process conditions and the yields of phosphine are given in Table 3, which shows that comparatively concentrated aqueous solutions, mainly of phosphoric acid, are most often employed as the electrolyte. Only in one case was the employment of an aqueous sodium chloride solution described [74] and it was noted that sodium hypophosphite was formed together with phosphine.

In all cases the electrolysis is carried out at elevated temperatures (between 50° and 120°C). Usually comparatively low current densities are stated (in the range 50–300 A m^{-2}). Ceramics, tantalum, titanium, rubber, and polyethylene are employed as constructional materials for the electrolysers. Judging from later patents [129-132], the electrochemical preparation of phosphine has encountered considerable difficulties in attempts to achieve a continuous process. It appears that the most serious are the following: rapid loss of reducing activity by the cathode; the adhesion of phosphorus to the surface of the cathode leading to an increase of voltage in the electrolyser; contamination of the electrolyte; blocking of diaphragm pores. The aim of the improvements to the process described in the patents is to eliminate the phenomena listed above.

In order to stabilise the activity of the electrode, it is suggested that bismuth, cadmium, and mercury salts be added to the electrolyte, whereby the yield of phosphine can be raised to 92–92%. In one patent [75] it is recommended that the electrolysis be carried out in the presence of lead ions which are generated by a periodic replacement of the

Table 3. Effect of electrolysis conditions on the yield of phosphine.

Cathode material	Anode material	Diaphragm material	Electrolyte	Current, A	Current density, A m^{-2}	Voltage, V	Yield of phosphine, %	Duration of expt.	t, °C	Gas flow rate, ml min^{-1}	Remarks	References
Wood's alloy	graphite	porous glass	sat. NaCl soln.	1	220	18	50	—	80	8	5% of sodium hypophosphite formed in catholyte	74
Wood's alloy	graphite	porous glass	40% H_3PO_4 soln.	1	—	7	92.5	—	85	7.3		126
Pb	Pb, Pt, PbO_2	ceramic, glass, resin	40% H_3PO_4 soln.	0.5	60—200	2.9—3.4	80—90	1 day	75—85		pre-electrolysis, addition of bismuth salts	73, 121, 122, 75, 76
Pb	Pt	ceramic	18% H_3PO_4 soln.	3	—	18.7	60	—	85	17.9		124
Pb	PbO_2	resin	ethanol with phosphorus	0.2—1	—	13—46	42.5	—	65			123
Pb	graphite	alundum covered by glass fabric	6—10% HCl 0.05% Pb	—	—	4	70—85	—	50		40-50% of cathode gas passed into catholyte	131
Pb	graphite	porcelain	6% HCl 0.05% Pb	—	258	—	90—95	—	85		cathode has 1.59 × 1.59 ribs 3.18 mm deep	132
Pb–Bi or Sn–Bi alloy	Pt, Sn	ceramic	40% H_3PO_4 soln.	0.5	260	0.9	90	6 days	74		alternate replacement of platinum anode by tin anode	75
Ni(77%)–Cu(4.8%)–Cr(1.5%)–Fe(14.9%) alloy	Pt	ceramic	40% H_3PO_4 soln.	0.5	—	2—3	85	16 days	95		4 ml of 10% lead acetate soln. added	75
Hg	Fe, Pt, Pb, graphite	glass, alundum	18–40% H_3PO_4 soln.	0.5—5	—	6—10	80—95	30 h	69—90		cadmium added to catholyte	73, 121, 122, 77, 125, 126
Hg	graphite	none	40% H_3PO_4 soln.	3	—	10	70	—	85			127
Zn	Fe	glass	4 M H_3PO_4 soln.	—	80—300	—	83.1	—	—			73, 121, 122

platinum anode by a lead anode. This modification increases the stable yield of phosphine to about 85%.

In all the examples quoted it is noted that, after prolonged operation, loose spongy deposits are formed on the cathode, which increase the electrical resistance of the electrolyser and, since part of them crumble away, they contaminate the phosphorus present in the solution. A special design of the electrolyser has been described[78], in which the cathode is located above the anode. According to the authors of the patent[78], in this case deposits are formed on the upper side of the electrode and do not hinder the passage of current. A special device has been described with the aid of which it is possible to remove continuously part of the catholyte and phosphorus to free them from contamination. Finally, an unusual form of cathode is recommended. The cathode should have ribs, projections, and channels. It is not clear from the patent data how a cathode of this shape prevents the formation of loose deposits.

To achieve the best contact between the electrode and phosphorus, the cathode should either touch the layer of fused phosphorus at the bottom of the electrolyser, or the phosphorus should be introduced in amounts such that its thickness on the cathode does not exceed 0.7 mm.

To prevent the blocking of the pores of the diaphragm, it is recommended that the latter be covered by a layer of polyethylene or another material which is not wetted by phosphorus[129,130]—fibreglass, plastics, graphite, etc. In one patent[77] it is suggested that the level of the anolyte be maintained above that of the catholyte, whereupon hydrostatic pressure will prevent the adhesion of phosphorus to the diaphragm.

One of the methods for reducing the adhesion of phosphorus consists in the introduction into the electrolyte of hydrocarbons, hydrogen, or cathode gas containing hydrogen[131]. On dissolving in phosphorus, these substances reduce its viscosity and hence the possibility of its adhesion to the diaphragm and to the walls of the electrolyte. A noteworthy application of a catholyte mixed with organic solvents in different proportions has been described[123]. It is asserted that in this case the cathode gas does not contain phosphorus hydrides other than PH_3.

Various improvements in the electrolyser design (for example, use of a carbon cathode, when there is no need for a diaphragm) are proposed in patents[125-128]. However, despite these improvements, optimum conditions for the electrochemical synthesis of phosphine have probably still not been found.

Recently studies were made[57-133] to determine favourable conditions for the electrochemical preparation of phosphine in aqueous solutions. It was established that the optimum conditions are as follows: current density of the order of 1800–2000 A m^{-2}, temperature 75–85°C, and a zinc cathode in solutions of 40% phosphoric acid. Under these conditions the current yield of phosphine (and the yield with respect to the phosphorus employed) reaches 65%. In contrast to the data of other patents[74-78,121-132], it is then unnecessary to use special devices for the circulation and purification of the catholyte and phosphorus, for coating the diaphragm, etc.

The mechanism of the electrochemical reduction of phosphorus has been investigated in fair detail for the mercury cathode[134,135]. It was established that phosphorus in aqueous ethanol solutions is reduced by mechanism with addition of twelve electrons per molecule:

$$P_4 + 12H^+ + 12\,e^- \rightarrow 4PH_3\,.$$

In aprotic media the process takes place by the addition of two electrons with formation of an anion and subsequent protonation of the latter[136]. The study of the reduction at a pendant mercury drop showed[135] the intermediate formation of a chemisorbed P_4Hg_X complex and in this respect the electrochemical reduction of phosphorus is analogous to the reduction of sulphur. Electrochemical reduction of phosphorus at a lead cathode is complicated by the formation of an intermediate phosphorus hydride[57].

A method for the preparation of phosphine and other volatile hydrides (silicon, boron, etc. hydrides) has been described recently[67,137-139]. The essential feature of the process is the electrolysis of fused lithium chloride, the lithium formed at the cathode reacting with the hydrogen supplied to the cathodic compartment forming lithium hydride; the latter passes to a separate chamber, where it reacts with phosphorus trichloride:

$$3\,LiH + PCl_3 \rightarrow PH_3 + 3\,LiCl\,.$$

The process is carried out at a temperature such that the phosphine formed is thermally stable. The chlorine evolved at the anode is used to prepare fresh portions of phosphorus trichloride. The design of the electrolyser provides for the elimination of contact between the phosphorus trichloride and the alkali metal to avoid the formation of free phosphorus.

A cell design has been developed for periodic and continuous operation. The anodic and cathodic compartments are separated either mechanically or a zone of "frozen melt" is set up in the middle. The anode and cathode are both made of graphite. This may be regarded as a method for the indirect chemical preparation of phosphine.

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It follows from the foregoing that phosphine has already found practical applications and that their range is being continuously extended. In this connection the development of rational methods for the preparation of phosphine on an industrial scale is assuming increasing importance. Comparison of the various methods for the synthesis of phosphine shows that the only procedure which has found practical application hitherto, despite its disadvantages, is the decomposition of metal phosphides. Although it is being tested under experimental industrial conditions[141], the synthesis of phosphine by the reaction of phosphorus with steam is scarcely likely to prove economical in view of the considerable consumption of phosphorus in the formation of phosphorus acids.

The most promising is the electrochemical method but its application has encountered certain difficulties, which, judging from the literature data, have not been resolved.

The chemistry of other phosphorus hydrides has been hardly investigated and probably the time is now ripe for systematic research in this field.

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Uspekhi Khimii

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Present-day State of the Theory of Bimolecular Reactions

E.E.Nikitin

Various simple models of bimolecular reactions are discussed which provide a qualitative interpretation of the principal aspects of the elementary act in the redistribution of atoms. The limitations imposed by the law of the conservation of total angular momentum have been elucidated for processes involving the intermediate formation of long-lived complexes. The limiting cases of the mechanisms of dislodgment and stripping have been examined for direct processes. The latter mechanism is interpreted in terms of an optical model. A list of 38 references is included.

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1. INTRODUCTION

The Review discusses the most recent development of the theory of bimolecular reactions, i.e. processes of the type

$$X + Y \rightarrow Z + U \qquad (1.1)$$

occurring in the gas phase. Since elucidation of the mechanism of this process is based in general on solving a many-body (in the simplest case the three-body) problem, the modern theory of bimolecular reactions is largely governed by progress in computational technique. Analysis of the trajectories of the representative point has yielded important results on the energy dependence of reaction cross-sections, on the energy distribution function of the reaction products, and on the angular distribution of elastically and inelastically scattered particles. Another line of research is based in large measure on models of the mechanism of the redistribution of particles and on certain hypotheses concerning the interaction of reactant molecules. This approach enables the final results to be obtained without complicated intermediate calculations, and thus permits several redistribution processes to be interpreted (if this is possible) in terms of relatively simple models. The most widely used are discussed below.

These models are most conveniently classified according to the extent to which the energy of the unstable molecular system formed on collision is able to undergo redistribution among the various degrees of freedom before the reaction can be regarded as complete. On the basis of these considerations the following classification is useful.

1. Reactions involving an intermediate complex. In these processes the mechanism of the redistribution of energy approaches a statistical process.
2. Direct reactions. According to the way in which the particles are redistributed, these are subdivided into three subgroups—(*a*) rebound mechanism, (*b*) mechanism of direct dislodgement, and (*c*) stripping or pick-up mechanism.

Several processes occurring by the above mechanisms will be examined in the present Review. We shall not in general be concerned with the rebound mechanism, since the chief advances in this field have been achieved by taking into account the simultaneous interaction of several atoms, this requiring the use of computers. Reactions having a rebound mechanism are usually considered in terms of the transition stage theory, and several problems for thermal reactions have been clarified in a previous review[1].

2. STATISTICAL THEORY OF REACTIONS. EXCHANGE OF ATOMS WITH FORMATION OF AN INTERMEDIATE COMPLEX

Discussion of General Formulation

The chief assumption in the statistical theory of bimolecular reactions is that the elementary act (1.1) takes place in two independent stages. The first stage involves formation of a complex or composite system XY*. In the second stage the complex XY* breaks down along all possible channels, the probability P of breakdown being calculated from the statistical theory of unimolecular reactions. It is clear that, for the assumed independence of the two stages to be valid, the lifetime τ of the composite system XY* should exceed substantially the characteristic times of the intramolecular motions. An estimate of τ can be obtained from the statistical theory of unimolecular reactions, which has now been quite well developed[2-4] and enables the mean lifetime of an active molecule before spontaneous breakdown to be calculated with satisfactory accuracy.

Let us suppose that the initial states of the molecules X and Y are characterised by a set of quantum numbers i. On formation of the complex the numbers i are supposed to lose their significance, the activated molecule being characterised by a new set of quantum numbers ϵ. Further, let the final products Z and U be characterised by the quantum numbers f. The cross-section of the elementary act is then written

$$\sigma_{if}(v_i) = \sum_{\varepsilon} \delta\sigma_{i\varepsilon}(v_i) P_{\varepsilon f}, \qquad (2.1)$$

where $\delta\sigma_{i\epsilon}$ is the cross-section of formation of the composite system XY* (or, as we shall call it, the capture cross-section of X and Y) in the state ϵ, and $P_{\epsilon f}$ is the probability of its breakdown along the channel f. The summation in Eqn. (2.1) is made over all states ϵ which can be formed from the initial state i. The symbol v_i denotes the initial relative velocity of the molecules X and Y.

The probability of breakdown $P_{\epsilon f}$ is given by the normalised partial rate of breakdown along the specified channel:

$$P_{\varepsilon f} = k_f(\varepsilon)/[k_1(\varepsilon) + k_{-1}(\varepsilon)] \qquad (2.2)$$

where

$$k_1 = \sum_f k_f(\varepsilon), \quad k_{-1} = \sum_i k_i(\varepsilon)\ . \qquad (2.3)$$

Here the summations with respect f and i are made over all channels in forward and reverse directions. The decomposition rate constants $k_n(\epsilon)$ of the active molecule $(XY^*)_\epsilon$ are in turn calculated from the theory of unimolecular reactions.

In classical mechanics the differential capture cross-section $\delta\sigma_{i\epsilon}(v_i)$ is given by the relation

$$\delta\sigma_{i\varepsilon}(v_i) = 2\pi b_i db_i \qquad (2.4)$$

where b_i is the impact parameter, which satisfies the condition $b_i < b_i^c$, while b_i^c is the maximum impact parameter at which capture takes place. In this formulation it is assumed, of course, that formation of the composite system does not involve surmounting a potential barrier, i.e. that the first stage in the reaction takes place with zero activation energy. The relation (2.4) is conveniently expressed in terms of the relative momentum l_i of the molecules X and Y:

$$\delta\sigma_{i\varepsilon}(v_i) = \frac{2\pi}{p_i^2} l_i dl_i, \quad p_i = \mu v_i\ . \qquad (2.5)$$

Although the condition of capture is most simply formulated by the requirement $l_i < l_i^c$, it is useful to introduce into (2.5), instead of l_i, the total momentum J of the system of colliding molecules, since it alone is a complete integral of the motion. Henceforward for simplicity we shall discuss the collision of an atom A with a molecule BC, so that the total angular momentum J is given by the vector sum

$$l_i + j_i = J \qquad (2.6)$$

in which j_i denotes the intrinsic momentum of BC.

Transformation from the variable l_i to the variable J (with j_i fixed) is most simply accomplished by means of the rules of vector addition[5,6]. As a result of this transformation the differential capture cross-section $\delta\sigma_{i\epsilon}$ is written

$$\delta\sigma_{i\varepsilon}(v_i) = \frac{2\pi}{p_i^2} \varphi(J; j_i, l_i^c) J dJ \qquad (2.7)$$

where the explicit form of the function φ has been given in a previous paper[6]. Here we note merely that φ vanishes when $J > j_i + l_i^c$. In order to determine l_i^c, we must formulate the conditions of capture. If the capture of A and BC takes place at sufficiently great distances, the main contribution will be made by the isotropic polarisation interaction $W(R) = q(R_0/R)^s$, and l_i^c then depends on the relative kinetic energy of the fragments[5-7]:

$$l_i^c(v_i) = (2\mu E_i R_0^s)^{1/s} \left(\frac{sq}{2E_i}\right)^{1/s} \left(\frac{s}{s-2}\right)^{1/s - 1/s} \qquad (2.8)$$

$$E_i = \mu v_i^2/2\ .$$

The energy E_i is subject, of course, to the limitations indicated below, which result from neglect of the contribution made by short-range forces[8].

We now specify the set of quantum numbers ϵ, on the assumption that the only integrals of motion of the composite system are the total energy E and the total angular momentum J[5-11]. Certain assertions must also be made concerning the electronic states between which a statistical redistribution of energy is possible. The probabilities of non-adiabatic transitions between these states are supposed to be sufficiently high for them not to limit the transfer of the representative point from one potential surface to another.

This last hypothesis cannot be regarded as valid for all reactions in which an intermediate complex is formed. Several ion–molecule reactions are now known whose very small cross-section is ascribed to the low probability of non-adiabatic transitions between the electronic states linking the initial and final terms of the partners[12].

The total cross-section σ_1 of reaction (1.1) can now be rewritten

$$\sigma_1(v_i) = \frac{\pi}{p_i^2} \int 2 J dJ \varphi(J; j_i, l_i^c) \frac{k_1(E, J)}{k_1(E, J) + k_{-1}(E, J)} \qquad (2.9)$$

where k_1 and k_{-1} are the rates of the spontaneous breakdown of ABC* in forward and reverse directions. In calculating the cross-section of reaction (1.1) into a specified channel (e.g. in a state having specified vibrational or rotational quantum numbers), we must replace $k_1(E,J)$ in the numerator of (2.9) by the corresponding partial rate constant. In most cases Eqn. (2.9) can be considerably simplified, since the relative momentum l_i usually exceeds appreciably the intrinsic angular momentum of the reactant molecules. In this case we can put $J \simeq l_i = p_i b_i$, and Eqn. (2.9) becomes

$$\sigma_1 = \frac{2\pi}{p_i^2}\int_0^{l_i^c} 2\, l_i dl_i \frac{k_1(E,J)}{k_1(E,J)+k_{-1}(E,J)} = 2\pi\int_0^{b_i^c} \frac{k_1(E,J)\, b_i db_i}{k_1(E,J)+k_1(E,J)} \quad (2.10)$$

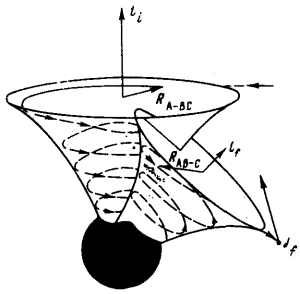

Figure 1. Energy surface for reaction involving an intermediate complex.

A reaction of this type can be represented diagrammatically by the movement of a representative point along potential-energy surfaces (Fig. 1). The relative motion of A and BC in the initial stage of capture takes place in a plane perpendicular to the relative angular momentum $\boldsymbol{l}_i$. If the energy axis lies in the direction of the vector $\boldsymbol{l}_i$, capture is represented by the trajectory described by the vector R_A–BC, as it descends spirally into the "funnel" corresponding to the potential W_{A-BC}. The representative point then reaches a region of strong interaction, where the redistribution of energy is described by statistical laws (shaded region). Finally, the representative point begins to rise along a second "funnel", which corresponds to the potential W_{AB-C} and whose axis lies in the direction of the vector of the relative motion of the products $\boldsymbol{l}_f$. The direction of the vector $\boldsymbol{l}_f$ is related to that of the intrinsic angular momentum j_f of the fragment AB and to the vector $\boldsymbol{J}$ by the conservation law $\boldsymbol{J} = \boldsymbol{l}_f + \boldsymbol{j}_f$.

If the dependence of the rates of decomposition k_1, k_{-1} on the total momentum $\boldsymbol{J}$ is neglected in the calculation of σ_1, formula (2.9) simplifies further to

$$\sigma_1 = \left[2\pi\int_0^{b_i^c} bdb\right]\frac{k_1(E)}{k_1(E)+k_{-1}(E)} = \sigma_1^{c_0}(v_i)\frac{k_1(E)}{k_1(E)+k_{-1}(E)} \quad (2.11)$$

where the first factor in the right-hand formulae gives the total capture cross-section, while second factor is the probability of breakdown in the forward direction.

Since the values of k_n are proportional to the number n of states in a channel, it is clear that the larger of the two constants k_1 and k_{-1} will be that which corresponds to the exothermic direction of the reaction. Let us assume for definiteness that reaction (1.1) is exothermic in the forward direction. Let us suppose further that the total energy E_1 of the initial state satisfies the condition $E_1 \ll Q$, where Q is the heat of reaction. Then the inequality $k_1 \gg k_{-1}$ will probably hold, and Eqn. (2.11) will give

$$\sigma_1 = 2\pi\int_0^{b_i^c} bdb = \sigma_1^c(v_i)\,. \quad (2.12)$$

Nevertheless, the cross-section σ_{-1} for the reverse reaction will contain the ratio $k_{-1}(E,J)/k_1(E,J) \ll 1$ following the integral sign. This ratio is proportional to the ratio of the number of open decomposition channels in reverse and forward directions. Provided that $E_1 < \hbar\omega$, i.e. when vibrations of BC cannot be excited on breakdown of the complex ABC*, the energetic dependence of σ_{-1} on the total energy of the partners AB and C near the threshold Q is described by the formula [8]

$$\sigma_{-1} = \text{const}\,(E-Q)^{s/2}\,. \quad (2.13)$$

This threshold dependence of the rate is related fundamentally to the law of the conservation of angular momentum. This can be seen from the argument that the first stage of the reaction involves formation of the composite system ABC*, the angular momentum of which is distributed within a certain range $0 < J < l_f^c$. On decomposition in the direction A + BC the maximum anular momentum j_i of the molecule BC is small, being determined by the excess of energy $E-Q$ over the threshold. On the other hand, l_i is also small for low values of E_i. This means that the vector sum of j_i and l_i is small, certainly much smaller than l_f^c. Thus only complexes having a small angular momentum $0 < J < l_i^c$ are actually able to break down in the direction A + BC. For complexes having $l_i^c < J < l_f^c$ only one type of decomposition is available—breakdown in the reverse direction: ABC* → AB + C.

Model Reaction $A_2^+ + A_2 \rightarrow A_3^+ + A$

As illustration of the statistical theory of bimolecular reactions we shall discuss an ion–molecule reaction of the above type. An actual example of such a reaction is the process

$$H_3^+(E_{i,n}) + H_2 \rightarrow H_3^+ + H + Q,\ Q = 1{,}1\ \text{eV} \quad (2.14)$$

in which the H_3^+ ions possess a specified vibrational excitation (quantum number n) and a relative kinetic energy E_1. The problem consists in calculating the cross-section σ of this reaction as a function of n and E_i.

Let us first consider the calculation of the total reaction cross-section for the ground state $n = 0$. An estimate based on a simplified form of the statistical theory [13] (disregarding the conservation of total momentum) shows that, with energy $E_i < 0.1$ eV, the rate of breakdown of the complex $[H_4^+]^*$ in the forward direction substantially exceeds the rate in the reverse direction. The cross-section of the reaction should then coincide with the capture cross-section σ^C, which in turn is given by the general formula (2.12) with the polarisation potential $W(R) = -\alpha e^2/2R^4$ (in which α is the polarisability of the neutral particle):

$$\sigma^c(v_i) = 2\pi e\sqrt{\frac{\alpha}{2E_i}},\ E_i = \mu v^2/2 \quad (2.15)$$

where μ is the reduced mass of the partners. An experimental investigation of the formation of H_3^+ ions (and of D_3^+

ions in the analogous reaction with deuterium) confirms the diminution in cross-section with increase in energy, the experimental absolute cross-sections being close to the theoretical values over the energy range investigated[15,16].

Let us now examine the dependence of σ on the vibrational quantum number n of the H_2^+ ion. In calculations based on the general formulae (2.9) it must be borne in mind that the initial angular momentum of this ion is quite small if it is produced by ionisation of low-energy H_2 molecules. Therefore the simplified formula (2.10) can be used to calculate σ_1, and for $n \neq 0$ the contribution of E_i to the total energy of the composite system $[H_4^+]^*$ can in general be neglected if $E_i < n\hbar\omega^+$ (where ω^+ is the vibration frequency of H_2^+). The cross-section σ_1 is conveniently written $\sigma_1 = \sigma^C P(E_{i,n})$, where $P(E_{i,n})$ is to be interpreted as the mean probability of reaction along the given channel. Different calculations of this factor[17,18] are difficult to compare directly, since the second was based on a simplified form of the theory[13], and took no account of identical channels of decomposition.

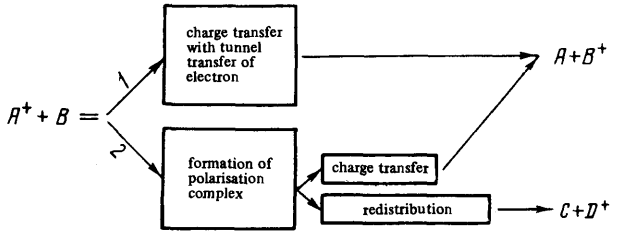

Figure 2. Competition between charge transfer with tunnel transfer of an electron, charge transfer with complex formation, and redistribution with complex formation.

Examination of the different cases of addition of the angular momenta of molecules resulting from breakdown of the composite system $[H_4^+]^*$ leads to the following estimate for the relative efficiency of decomposition in the forward direction with energy $E_i = 0.04$ eV[17]:

$$P(n=0):P(n=1):P(n=2):P(n=3):P(n=4) = 1:0.9:0.75:0.62:0.52. \quad (2.16)$$

This agrees qualitatively with the initial terms in the analogous series representing the experimental data[19]

$$1:0.5:0.4:0.5:0.0\ . \quad (2.17)$$

The discrepancy between theory and experiment, and in particular the inability of the statistical theory to explain the very marked decrease in probability of reaction for $n \geq 4$, are perhaps due to the breakdown of the main assumption of the theory, that a long-lived complex is formed at sufficiently high energies, and to the disregard of the effect of anisotropic interaction in determining the boundary between open and closed channels†. It must also be remembered that the experiment giving the series (2.17) was interpreted on the assumption that the Franck–Condon principle applied to the ionisation of H_2. It is possible, however, that this principle is not satisfied in the vicinity of the threshold[21].

In calculating the cross-sections of reactions between an ion and a molecule we must take into account the competition between the redistribution of particles and the transfer of charge[16,22]. An important aspect is that, as the kinetic energy increases, the charge-transfer cross-section diminishes more slowly than does the redistribution cross-section. Fig. 2 illustrates such competition in the case of resonance charge transfer. Along path *1* either the transfer of an electron by the tunnel effect or the formation of a polarisation complex is possible. The relative efficiency of these processes is proportional to the corresponding cross-sections, which in turn are determined by the critical values of the impact parameters.

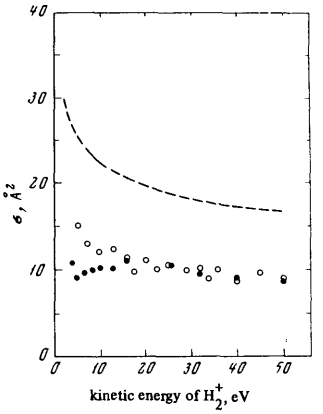

Figure 3. Charge transfer as one of the paths of the competing reactions (2.14) and (2.19). The broken curve shows the calculated charge-transfer cross-section, and the points represent experimental results.

Along branch *2* the relative efficiency of the two paths is now determined by the distribution of energy in the complex, depending mainly on the sign and magnitude of the energy evolved during the redistribution. In particular Markin and Tal'roze[23] investigated the reaction

$$H_2^+ + O_2 \rightarrow [H_2O_2^+]^* \begin{cases} HO_2^+ + H & (a) \\ O_2^+ + H_2 & (b) \end{cases} \quad (2.18)$$

which satisfies this condition. The ratio σ_a/σ_b of the cross-sections was found to diminish with increase in energy, and the cross-section of reaction (*a*) became very small at a relative energy of the ions of about 10 eV. This immediately shows that the lifetime of the composite system decreases with increase in energy, and ultimately the very concept of an intermediate complex becomes devoid of meaning.

Another example, from the work of Levental et al.[24], is illustrated in Fig. 3. The broken curve represents the calculated cross-section σ_{calc} of resonance charge transfer

$$H_2^+ + H_2 \rightarrow H_2 + H_2^+ \quad (2.19)$$

† Such anisotropy is most clearly apparent in reactions between an ion and a molecule having a dipole[20]. In this case the field of the ion retards the rotation of the molecule, and in the limiting case completely orients it in the direction of the line of collision, so that the classification of channels into closed and open should allow for interaction of the momenta l_i and j_i.

while the points give the experimental values of the cross-sections σ_{exp} for this process. The divergence between the two curves is due to reaction (2.14), which "cuts out" from the cross-section σ_{calc} the internal region σ_1 in such a way that $\sigma_{exp} = \sigma_{calc} - \sigma_1$.

3. THEORY OF DIRECT REACTIONS. MECHANISM OF DIRECT DISLODGMENT

Experimental investigation of reactions occurring in molecular beams shows that many exchange reactions, particularly those of alkali-metal atoms with halogen and hydrogen halide molecules, do not involve the formation of a long-lived intermediate complex: i.e. they take place by a direct mechanism. Henceforward we shall take "direct mechanism" to mean a mechanism of interaction of the partners in which the residence time in a volume of molecular dimensions is of the order of a few nuclear vibration periods or less. Fig. 4 shows the various possibilities for the redistribution of atoms in the simplest reaction A + BC → AB + C which has a direct mechanism. In the rebound mechanism A approaches BC, a chemical bond AB is formed, and then the atom C is repelled from the resulting molecule AB. As already mentioned, this situation is usually discussed in terms of the transition state theory.

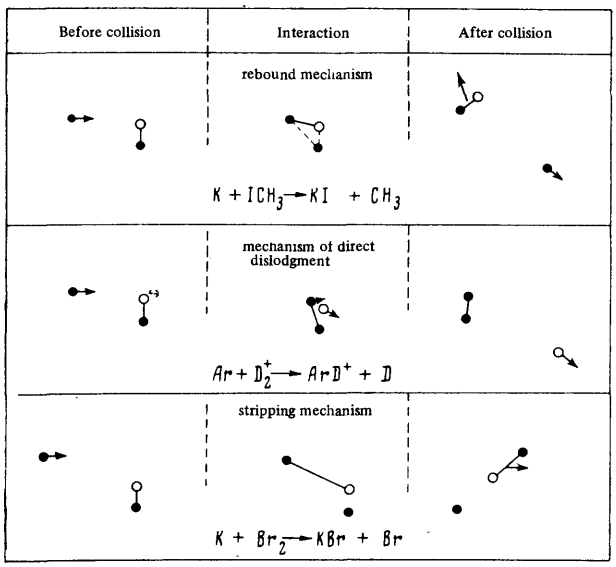

Figure 4. Diagrammatic illustration of rebound mechanism, mechanism of direct dislodgment, and stripping mechanism.

If a mechanism of direct dislodgment operates, the atom A dislodges the atom C from the molecule BC, is slowed down, and remains combined with the atom B.

With a stripping mechanism the atom A interacts mainly with atom B, and the interaction of A with C can often be neglected. The resulting diatomic molecule is scattered mainly in the direction of motion of the atom A.

Fig. 4 includes examples of reactions of the above types.

It is an extremely complicated theoretical task to calculate the cross-sections of such processes. However, the theory assumes a simple form when the time of interaction τ_{st} between the incident atom A and one of the atoms in the molecule BC can be regarded as small in comparison with the period of vibration of the initial molecule BC or the final molecule AB (the so called impulse approximation) [25-27]:

$$\tau_{st}\omega_{AB},\ \tau_{st}\omega_{BC} \ll 1 . \qquad (3.1)$$

An analytical expression can be obtained for the reaction cross-section if two additional conditions are introduced besides (3.1): it must be postulated that the amplitude of the pair scattering A_{XY} is far smaller than the interatomic distances in the molecules:

$$A_{XY} \ll R_{XY},\ X, Y = A, B, C \qquad (3.2)$$

and that the interaction potential U of three particles is additive in character:

$$U = U_{AB} + U_{BC} + U_{AC} . \qquad (3.3)$$

The pair potentials are completely arbitrary: the only limitation imposed on them is due to condition (3.1). It must be noted that the additive potential approximation (3.3) permits no description of a potential barrier or a region of breakdown, nor a region of transition from one surface to another. Therefore the approximation (3.3) can be applied only to reactions in which neither activation energy nor non-adiabatic effects play a significant part.

Condition (3.1) imposes a lower limit of 5–10 eV on the relative energy of the partners on collision. With such energies the exchange

$$A + BC \rightarrow AB + C \qquad (3.4)$$

begins to be subject to competition by the dissociation

$$A + BC \rightarrow A + B + C . \qquad (3.5)$$

The existing theory enables the reaction cross-sections for exchange σ_{exch} and dissociation σ_{diss} to be calculated with the quantum character of the motion of the nuclei in the intermediate and resulting molecules taken into account. Here we shall give merely a brief account of the classical form of the theory describing the broad features of the energy dependence of the cross-section in the range above the above lower limit [25].

Assuming for simplicity that the target molecule is at rest before collision, we shall consider that a stable molecule AB is formed if the relative energy E_{AB} of the atoms A and B after the dislodgment of C is less than the bond energy D_{AB}.

The starting point for deducing an expression for σ_{exch} is the formula for the differential cross-section of the loss of energy ΔE by the atom A incident with energy E on the stationary atom C. For a model of rigid spheres we have

$$d\sigma = \pi R_0^2 \frac{d\Delta E}{\Delta E_{max}},\quad \Delta E_{max} = E\frac{4\mu_{AC}}{m_A + m_C} . \qquad (3.6)$$

The energy E_{AB} of atom A after dispersions on C, expressed in the system of the centre of mass A–B, is

$$E_{AB} = (E - \Delta E)\frac{\mu_{AB}}{m_A} . \qquad (3.7)$$

Expressing $d\Delta E$ in Eqns. (3.6) in terms of dE_{AB}, and equating the differential retardation cross-section $d\sigma$ to the differential capture cross-section, we find that

$$d\sigma_{exch} = d\sigma(E_{AB}) = \pi R_0^2 \frac{m_A}{\mu_{AB}}\frac{dE_{AB}}{\mu_{AB}} . \qquad (3.8)$$

The total exchange cross-section is obtained from this by integrating with respect to dE_{AB}:

$$\sigma_{exch} = \pi R_0^2 \frac{m_A}{\mu_{AB}\Delta E_{max}} \left[\min \begin{Bmatrix} \frac{\mu_{AB}}{m_A} E \\ D_{AB} \end{Bmatrix} - \frac{\mu_{AB}}{m_A} (E - \Delta E_{max}) \right]. \quad (3.9)$$

Hence it follows that, when $E \leq D_{AB} m_A/\mu_{AB}$, the exchange cross-section is πR_0^2. This is clearly the case: right from the start the relative energy of A–C is such that every dislodgment of C enables a stable molecule to be formed. When $E > D_{AB} m_A/\mu_{AB}$, the exchange cross-section diminishes because the dissociation channel is opened:

$$\sigma_{exch} = \frac{\pi R_0^2}{4} \left[\frac{(m_A + m_C)^2 (m_A + m_B)}{m_A m_B m_C} \cdot \frac{D_{AB}}{E} - \frac{(m_A - m_C)^2}{m_A m_C} \right]. \quad (3.10)$$

When the energy has the value E^* at which the expression in square brackets vanishes, the exchange channel is completely closed, and every collision A + BC leads to the dissociation of BC.

The concepts of a mechanism of direct dislodgment cannot usually be applied, either to thermal reactions or to processes in molecular beams, if the kinetic energy of the partners does not exceed several tens of electron-volts. Nevertheless, this mechanism represents an important particular case in which a many-body problem reduces to a problem of pair interactions. The more exact quantum theory of reactions of direct dislodgment enables us to take into account the effects of repeated scattering, a sudden change in potential, preliminary rotational and vibrational excitation of the target molecule, and the dependence of the effective dissociation energy of the resulting molecule AB on its rotational state[26,27]. In particular, the quantum distribution of momenta of atoms in the vibrational ground state of the hydrogen molecule has been suggested to be responsible for the rapid fall in the cross-section of the reaction

$$Ar^+ + H_2 \rightarrow ArH^+ + H \quad (3.11)$$

in the energy range $E > E^*$, where according to classical views the cross-section of the process should have been precisely zero. A mechanism of direct dislodgment provides an explanation for the slower fall (with increase in energy) in the cross-section of the reaction

$$Ar + D_2^+ \rightarrow ArD^+ + D \quad (3.12)$$

than in that of the reaction

$$Ar^+ + D_2 \rightarrow ArD^+ + D \quad (3.13)$$

as a consequence of initial vibrational excitation[27]. Furthermore, a simple interpretation is given of the fact that the cross-section of formation of the ion ArH^+ in the reaction Ar + HD^+ exceeds that for formation of the ion ArD^+.[27]

However, the interpretation of the above reactions of direct dislodgment is not unambiguous. In many cases reactions of this type can be successfully described in terms of a stripping model[12,28,29]. Nevertheless, a mechanism of direct dislodgment should always be considered as a possible mechanism at high collision energies, especially as it permits of relatively simple theoretical treatment.

4. THEORY OF DIRECT REACTIONS. MECHANISM OF STRIPPING

Let us now discuss another type of reaction, taking place by the so called stripping mechanism. This term applies to reactions in which an incident atom A interacts mainly with the atom in the molecule BC which is directly involved in the exchange‡. The interaction of A with C in reaction (3.4) can be neglected, for example, in rapid collisions where the time of interaction of A with B is less than the time required for substantial transfer of momentum from B to C. It is possible that processes of this kind, together with those of direct dislodgment, play a part at energies exceeding 5–10 eV. With ordinary thermal reactions (below 10 000°K) the relation between the collision time and the time of intramolecular vibrations is such that there can be no question of impulse interaction of A with B. Nevertheless, there exist certain types of reaction, even at low energies, whose formal characteristics satisfy the conditions of stripping. The cross-section of these reactions is usually very large ($\sigma \geq 100$ Å), and the resulting diatomic molecule is scattered mainly ahead relative to the direction of motion of the atom A. Since large cross-sections indicate that detachment occurs at large impact parameters ($b > 6$–7 Å), a model having a short-range potential (e.g. a rigid-sphere model) cannot be used to interpret these reactions.

Examples of processes of this type are provided by the reactions

$$M + X_2 \rightarrow MX + X \quad (4.1)$$

where M is an alkali-metal atom and X a halogen atom. A "spectator–stripping" model describes approximately the kinetics of such reactions, the M atom stripping an X atom from the X_2 molecule, while the momentum of the other X atom remains almost unchanged. A suggested interpretation of the dynamics of these reaction[30–32] starts from a mechanism of "harpooning", in which the first stage of the process involves dissociative charge transfer, and the second stage the formation of a bound ion-pair:

$$M + X_2 \rightarrow M^+ + X_2^- \rightarrow M^+ + X^- + X \rightarrow M^+X^- + X \rightarrow MX + X \quad . \quad (4.2)$$

The first stage—charge transfer—is the only inelastic process occurring at large distances, so that elastic processes make the chief contribution to scattering without redistribution of particles. The fact that all non-elastic channel without particle redistribution can be excluded from consideration enables the reaction and the elastic scattering to be described relatively simply in terms of a so called optical model. This model consists essentially in replacing the actual potential $W(R_{X_2-M})$, which leads to elastic scattering, by a complex potential[33] (R_{X_2-M}), the imaginary part of which (in a quantum treatment of the process of scattering) is responsible for partial absorption of the scattered particles. This absorption, which is shown in a weakening of the beam of incident particles, must be attributed, of course, to the reaction. If the elastic scattering of particles can be interpreted in terms of an optical model, therefore, it will give direct information on the probability of reaction as a function of the impact parameter. While describing reaction as absorption of the initial particles, an optical model, of course, will give no indication of the way in which energy is distributed among the degrees of freedom of the reaction

‡ The distinction between a model of direct dislodgment and a stripping model is most simply explained by comparing the limiting energies E^* of the incident atom A at which the exchange channel is closed. For the former case

$$E^* = \left(\frac{m_A + m_C}{m_A - m_C}\right)\left(\frac{m_A + m_B}{m_B}\right) D_{AB}$$

and for the latter

$$E^* = \left(\frac{m_A + m_B}{m_B}\right) D_{AB}.$$

products. In this sense it will give less information on the reaction than will detailed dynamic models. However, it possesses the advantage that it permits a simple interpretation of elastic scattering in terms of an interaction potential and an interaction responsible for charge transfer.

An energy diagram illustrating dissociative charge transfer is shown in Fig. 5. On the right are depicted the terms of the molecule X_2 and the ion X_2^- (internuclear distance r) when the intermolecular distance R is infinite. The left-hand side of the diagram shows the terms as a function of R. Term *1* corresponds to effective interaction of X_2 and M in the initial state with a fixed angle γ between the vector R and the molecular axis r of the molecule X_2. At great distances, which are of interest in the present problem, this interaction $W_C(R)$ is characterised by weak attraction. When the centrigual energy is taken into account, however, the effective potential $W_{C,\mathrm{eff}}(R) = W_C(R) + l^2/2\mu R^2$ represents repulsion. The set of effective ionic terms $W_i(R)$ corresponds to Coulombic attraction. For every energy ϵ reckoned from the level of the separated system $X_2(n = 0) + M$ there is a corresponding term $W_i(\epsilon,R)$, and $W_{\mathrm{eff}}(\epsilon,R) = W_i(\epsilon,R) + l^2/2\mu R^2$. Among them Fig. 5 shows the boundary of the continuous spectrum *2* ($\epsilon = \epsilon_0$), term *3* corresponding to a vertical transition ($\epsilon = \epsilon^*$), the boundary of the Franck–Condon region *5* ($\epsilon = \epsilon^* - \Delta\epsilon$), and *6* ($\epsilon = \epsilon^* + \Delta\epsilon$), one of the terms of the continuous spectrum *4* (arbitrary ϵ).

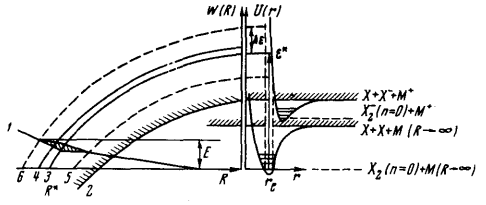

Figure 5. Electronic and vibrational terms involved in the dissociative charge transfer $M + X_2 \rightarrow M^+ + X^- + X$.

Interaction between covalent and ionic states can be described in different ways. Firstly, we can speak of non-adiabatic transitions between the covalent term and a continuous system of ionic terms. Secondly, we can speak of a broadening of a covalent term immersed in a continuum of ionic terms, and of conversion of a stationary into a quasi-stationary state. The second interpretation is illustrated in Fig. 5, where the covalent term *1* is shown broadened within the Franck–Condon region.

Let us suppose that the breakdown of each vibrational state of the molecule X_2 in the region $R \simeq R^*$ can be considered independently, and that the relative motion of X_2 and M can be described by means of classical mechanics. The first of these postulates permits a substantial simplification of the general problem, by reducing it actually to a two-body problem. The possibility of the independent description of dissociations arises only if, during passage through the Franck–Condon region, the interaction X_2–M does not induce vibrational transitions between the levels of X_2 (condition that the collisions shall be adiabatic) and if the interaction is sufficiently weak in absolute magnitude for no overlapping of the broadened vibrational levels of the X_2 molecule to occur in the region $R \simeq R^*$. These conditions can be written

$$\omega(X_2)\,\tau_{st} \gg 1 \qquad (4.3a)$$

$$\bar{\Gamma}_n/\hbar\omega(X_2) \ll 1 \qquad (4.3b)$$

where τ_{st} denotes the characteristic time of traversal of the Franck–Condon region, while $\bar{\Gamma}_n$ is the mean width of the vibrational level at $R \simeq R^*$. When conditions (4.3) are satisfied, the probability of dissociation of every level can be calculated by means of the formulae of the quasi-stationary adiabatic approximation

$$P_n = \exp\left[-\frac{1}{\hbar}\int_R \Gamma_n(R)\,dt\right] \qquad (4.4)$$

This approximation forms the basis of the so called optical model in stripping reactions [33–38]. Formula (4.4) gives the attenuation of a beam of elastically scattered particles moving along the trajectory $\mathbf{R} = \mathbf{R}(t)$. A rough estimate of the exponential (4.4) yields

$$\frac{1}{\hbar}\int \Gamma_n(R)\,dt = \frac{\bar{\Gamma}_n\tau_{st}}{\hbar} = \left(\frac{\bar{\Gamma}_n}{\hbar\omega}\right)(\omega\tau_{st}) \qquad (4.5)$$

We can see that conditions (4.3) do not restrict the value of this integral (4.5): the first factor on the right-hand side is small, while the second is large. This means that, to the approximation of independent vibrational states, a case of considerable absorption is possible, i.e. a relatively high probability of reaction. It is clear that, with sufficiently large impact parameters, the relations (4.3) will always be satisfied. However, the total contribution of those collisions for which the condition of relatively strong absorption $\bar{\Gamma}_n\tau_{st}/\hbar > 1$ is satisfied as well as conditions (4.3) will depend on the features of the interaction responsible for charge transfer.

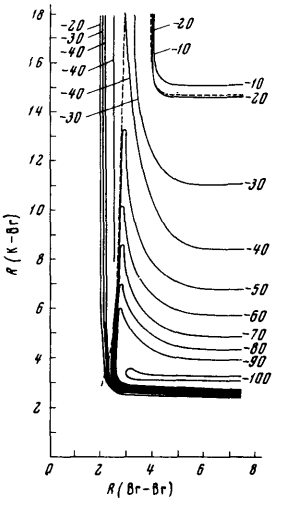

Figure 6. Energy surface for the reaction $K + Br_2 \rightarrow KBr + Br$ constructed by adiabatic mixing of covalent and ionic terms [32].

Infringement only of the first of the two conditions (4.3) implies that the channel of vibrational excitation can compete with the dissociation channel. If only the second condition is infringed, the probability of vibrational excitation is low, but the mutual influence of different vibrational states of the covalent electronic term must be taken into

account in calculating the probability of transition. However, these conditions are not fundamental, in the sense that an approximate solution of the problem can still be obtained from a consideration of two interacting particles. If neither of the conditions (4.3) is satisfied, the problem of calculating the cross-section, both of elastic scattering and of scattering accompanied by reaction, reduces to the general three-body problem, where we need consider only the one electronic term arising from the adiabatic mixing of both covalent and ionic states. The principal characteristics of the potential energy of a system for which a covalent state and an ionic state are fundamental are illustrated in Fig. 6. Here we note the main features of the motion of the representative point along a surface of this type. The presence of a sharp break on the surface, corresponding to transition from a covalent state to an ionic state of the partners, is very vividly illustrated by the concept of an "electronic harpoon"[30-32]. The atom M approaches the molecule X_2, and at quite a large distance, when the relative motion of the neutral pair M and X_2 can still be regarded as free, an electron passes from the atom M to the molecule X_2. After the electronic "harpoon" has linked the pair M^+ and X_2^- by Coulombic attraction, rearrangement of the system is possible, resulting in formation of the pair M^+X^- and X. The actual process of rearrangement can take place in various ways. In particular, the electronic term of the system X_2^- may correspond to an unstable state. If the time required for dissociation of the ion were short compared with that during which the distance between M^+ and X_2^- changed significantly, the angular distribution of the particles and the energy distribution could be calculated formally from the conservation laws for momentum and for energy. In contrast to a true stripping reaction, however, these relations should have also taken into account the change in energy and relative momentum of the pair X_2^- occurring on non-adiabatic transition of the X_2 molecule from a neutral to an ionic state. These ideas have been used to interpret experiments on the reactions of potassium, rubidium, and caesium atoms with bromine and iodine molecules[32]. If dissociation of the ion cannot be regarded as instantaneous, the general problem cannot be divided into a set of two-particle processes, and its solution requires explicit consideration of the interaction of three particles. In this way we arrive at the general problem mentioned in the Introduction.

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Institute of Chemical
Physics, Academy of
Sciences, Moscow USSR

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Some Aspects of the Kinetics of Molecular Reactions

F.B.Moin

Experimental data on the kinetics of elementary gas-phase reactions undergone by molecules are reviewed. The classification of reactions is discussed on the basis of the structure of activated complexes. Reaction mechanisms of various types are analysed in detail. The activation energy is shown to be determined additively mainly by activated bonds: the presence of substituents, which play no direct part in the reaction, has little effect on the activation energy. An analysis is made of the effect of conjugated and cumulative π-bonds in the activated complex on the activation energy. Conjugation and cumulation substantially lower the potential barrier to reaction. A list of 206 references is included.

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I. INTRODUCTION

In the present paper the term "molecular reactions" will imply those elementary reactions where the initial systems and products contain only *molecules*—not atoms, radicals, or biradicals.

Investigations of molecular reactions occupy an important place among the numerous papers on the kinetics of elementary reactions which have been published to date. Nevertheless, these results have not been summarised and systematised to the same extent as has been done for the reactions of atoms and radicals. The reasons for this are the considerably greater qualitative diversity of elementary molecular reactions and the far less complete theoretical study that has been made of them because of their greater complexity.

Actually, in the commonest and most thoroughly studied radical substitutions of the type $R + R'X \rightarrow RX + R'$ only one chemical bond is broken, and the transition state has an extremely simple structure. In thermal decompositions of molecules into two atoms or radicals, of the type $R-R' \rightarrow R + R'$, too, only one chemical bond is broken, while the potential barrier to reaction is given by the energy of rupture of the bond R–R'. Radical reactions of this type have been the subject of quite full theoretical study.

A characteristic feature of molecular reactions is that they involve the cleavage of more than one chemical bond, while the activated complex has a more complicated structure. Nevertheless, kinetic investigations of molecular reactions are usually made on a particular restricted class of reactions, and very little attempt has been made to establish an interrelationship between and general laws for the kinetics of molecular reactions belonging to different classes.

The present Review represents an attempt to summarise, analyse, and systematise published information on the kinetics of molecular reactions, the starting point being the additive method for calculating the activation energies of chemical reactions which I have developed[1].

II. CLASSIFICATION OF REACTIONS

A rational classification of elementary reactions is of paramount importance for the analysis and generalisation of kinetic data. It is advisable to base such a classification on the structure of the activated complexes, which reflects most profoundly all the fundamental kinetic features of the reactions.

Szabó[2] worked out a possible classification based on the structure of the activated complexes. It contains a total of 23 different types of reactions and the same number of empirical coefficients for calculating the activation energy. A fundamental defect of this classification is that in many cases forward and reverse reactions are of different types, in spite of the obvious identity of the corresponding activated complexes. As a consequence, the difference between the activation energies of forward and reverse reactions, calculated by Szabó's method, is not in general equal to the heat of reaction, as it should be in reality.

The classification of chemical reactions which I have proposed is also based on the most fundamental features of the structure of the corresponding activated complexes. As before[1] an activated complex is regarded as a molecule whose atoms are combined with one another not by chemical but by weaker, "activated" bonds. Since each activated bond corresponds to a definite chemical bond in the initial system or in the reaction products, the number of activated bonds is given by the sum of the numbers of chemical bonds cleaved N_{cl} and formed N_f:

$$N^{\neq} = N_{cl} + N_f.$$

Table 1 lists the main types of activated complexes. An activated complex of any type is the same for forward and reverse reactions. The only difference between the latter is that formed and cleaved bonds interchange roles. Other activated complexes are also possible, e.g. seven-membered, eight-membered, etc. complexes. However, these are encountered considerably more rarely in the reactions under investigation. This classification covers not only molecular but also radical and biradical reactions.

Analysis of numerous experimental data on the mechanisms of reactions whose molecular character has been established shows that they nearly all involve the formation of either four-membered or six-membered activated complexes†.

† Except for *cis–trans* isomerisations involving an activated complex having $N^{\neq} = 1$. For the mechanism of these reactions see Section IV, 1.

In cases in which the reaction mechanism cannot be represented by the above complexes, there are usually sound reasons for supposing that the reaction is not elementary, but passes through several stages (not excluding the intermediate formation of radicals, for example).

Table 1. Classification of activated complexes.

$N^{\neq}$	N_{cl}	N_f	Structure of activated complex
1	1 0	0 1	A...B
2	1	1	A...B...C
3	2	1	A···B...C...D
	1	2	A...B ·C·
4	2	2	A...B D...C
5	3	2	A...B E·C·D·
	2	3	
6	3	3	A...B F C E...D

Table 2. Mean energies of bonds in molecules (Q) and in activated complexes ($Q^{\neq}$) at 0°K (kcal)*.

Bond	Q, kcal	$Q^{\neq}$, kcal
H—H	103	48
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	27
π-C—O (in aldehydes and ketones)	88	18
π-C—O (in acids)	124	45
O—H	105	55
σ-C—N	66	11
N—H	92	25
C_{prim}—Cl	76	18
C_{sec}—Cl	76	25
C_{tert}—Cl	76	32
C_{prim}—Br	63	16
C_{sec}—Br	63	21
C_{tert}—Br	63	26
C_{prim}—I	47	8
C_{sec}—I	47	16
C_{tert}—I	47	24
H—Cl	102	40
H—Br	87	33
H—I	70	23

* Here and subsequently we shall for brevity write "kcal" instead of "kcal mole^{-1}".

Note. Correction for conjugation $\Delta Q^{\neq}_{conj} = 12$ kcal; correction for cumulation $\Delta Q^{\neq}_{cum} = 8$ kcal.

An important characteristic of activated bonds is that their mean energy is about the same in different activated complexes. Table 2 gives values of mean bond energies in molecules and activated complexes, from which it is easy to calculate the activation energy of a chemical reaction by means of the additive principle

$$E = \Sigma Q - \Sigma Q^{\neq} \qquad (1)$$

where Q and $Q^{\neq}$ are the mean energies of a bond in a molecule and in an activated complex respectively.

A more detailed account of the method of calculation will be found in the previous review[1]. Table 2 has been somewhat expanded and refined in comparison with the corresponding previous table[1]; in particular, the bond energies for nitrogen have been added, and also a correction $\Delta Q^{\neq}_{cum}$ for the effect of the cumulation of three or more π-bonds in a chain.

If a reaction involves cleavage of cyclic bonds, one energy of rupture of a carbon–carbon bond in the ring (50, 60, and 72 kcal respectively for cyclopropane, cyclobutane, and cyclopentane) is substituted in Eqn. (1) and also the corresponding energy of an activated bond (4, 12, and 22 kcal for the same rings).[1]

Before surveying published information, we must comment on experimental methods for studying the kinetics of molecular reactions.

III. METHODS OF STUDYING THE KINETICS OF MOLECULAR REACTIONS

In principle the determination of the rate constants of molecular reactions is considerably simpler than of radical or ionic reactions, since the concentrations of all the species involved can easily be measured. Nevertheless, methods for the study of molecular reactions have several peculiarities, associated not so much with determining the rate constants as with proving that the measured constants do relate to the given elementary processes. The reaction under investigation is sometimes complicated by several side-reactions, and this makes an unambiguous interpretation of the results considerably more difficult. The complications met most frequently are due to the occurrence of heterogeneous and radical–chain processes.

Heterogeneous Reactions

Many molecular decompositions and isomerisations are extraordinarily sensitive to the condition of the walls of the reaction vessel. The effect of the walls on reaction velocity may have several causes. The first possibility to be borne in mind is heterogeneous catalysis of the reaction by the walls. Such reactions as hydrogenation and dehydrogenation, for example, can easily be catalysed by various surfaces, especially metallic surfaces. Apparently the wall also catalyses the decomposition of certain alkyl halides (e.g. ethyl chloride[3,5]). In several cases the rates of the homogeneous reaction and of the catalytic reaction on the wall are comparable. In other cases the reaction takes place almost solely on the wall (e.g. the decomposition of ammonia[4]).

The relative rates of homogeneous and heterogeneous (catalytic) reactions is determined by several factors, including the nature and the state of the surface, the ratio of the surface area of the vessel to its volume S/V, and the experimental conditions (temperature and pressure). Heterogeneous catalytic decompositions usually have lower activation energies than the homogeneous reactions, so that the relative contribution of the heterogeneous reaction diminishes with rise in temperature.

In the kinetic study of molecular reactions the occurrence of heterogeneous reactions is usually detected by making experiments at different S/V ratios, and also by special treatment of the surface of the reaction vessel.

The latter effect is often achieved by "aging", i.e. by making a large number of experiments in the same vessel. This quite often improves the reproducibility of the results. "Aging" is explained by the appearance on the walls of a thin film of carbon deposits, which are inert towards the given reaction.

Heterogeneous reactions can be entirely eliminated by a special technique[5] for studying the kinetics of first-order reactions in a stream of an inert gas, which completely prevents reactant molecules from striking the walls of the reaction vessel. In this technique the reaction is conducted under streamline flow conditions in the initial (diffusion) portion of the zone in which a current of the reactant mixes with an accompanying coaxial flow of the inert gas. By this means kinetic measurements are made only on the homogeneous reaction.

Heterogeneous reactions can be eliminated also by means of a shock tube, which has recently become widely used. In this method a detonation wave effects rapid heating of the initial gaseous mixture, while the walls of the vessel remain cold.

Radical-Chain Processes

Molecular reactions are often complicated also by radical-chain processes, and therefore methods for the detection and suppression of radical reactions are of primary value. The most convincing evidence for the participation of free atoms and radicals in a reaction is their direct detection and measurement of their concentrations. Various physical and chemical methods (electron spin resonance, mass spectrometry, the mirror technique, etc.) are used for this purpose. In the study of molecular reactions, however, it is not so important to detect radicals as to prove their absence. This is a more complicated task, since a failure to detect radicals still does not mean that there are absolutely none in the system. Nevertheless, the inhibition method, consisting in adding substances which can react readily with radicals and thereby remove them from the system, has become widely used for assessing the possible part played by radical processes. The most frequently used inhibitors are nitric oxide, propene, toluene, and cyclohexene. If the rate of a reaction is not affected by the addition of inhibitors, this is regarded as an argument in support of its molecular character. Even when an inhibiting effect is present, it is sometimes considered that the "residual" inhibited reaction is molecular, since secondary radical processes are then completely suppressed.

To ascertain the possible effect of heterogeneous and radical processes on the kinetics and the mechanism of molecular reactions it is now standard practice to conduct experiments at various S/V ratios and also with additions of inhibitors, and if no appreciable change in reaction velocity is detected, it can be more or less confidently stated that the reaction is molecular.

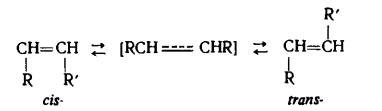
Careful analysis of the reaction products and the use of isotopes are extremely useful in the detection of radical processes. When radicals are present, many secondary products are usually formed. If, however, the reaction is conducted in a mixture, say of an undeuteriated and a completely deuteriated reactant, radical reactions will yield partly deuteriated products. In the absence of free radicals the products of the reaction should be either undeuteriated or completely deuteriated compounds. This method is applicable, of course, only to decompositions and isomerisations, and only if no deuterium exchange takes place either between molecules of the initial reactant or between molecules of the reaction products.

However, it must be borne in mind that short-lived biradicals can sometimes take part in a reaction, these being able to isomerise into molecules in a time less than that between collisions. In this case attempts to detect such biradicals by means of inhibitors will be unsuccessful, but this does not prove their absence. Additional difficulties are thereby created for the experimental investigation of the reaction mechanism. Determining the stereochemical structure of the reaction products may prove of some assistance here, since molecular reactions, unlike radical reactions, are usually stereospecific.

IV. ANALYSIS OF EXPERIMENTAL DATA

1. *cis–trans*-Isomerisation of Ethylenic Compounds

The *cis–trans* isomerisation of ethylenic compounds is the only example of a molecular reaction whose activated complex contains a single activated bond:



cis- *trans-*

The activation energy of reactions of this type, calculated additively, is

$$E = Q_{\pi\text{-C=C}} - Q^{\neq}_{\pi\text{-C=C}} = 61-17=44 \text{ kcal} .$$

Certain existing experimental values would appear to agree fairly well with this calculation, as can be seen from Table 3.

Table 3. Experimental values of the activation energy and of the logarithms of the pre-exponential factor for the *cis–trans* isomerisation of alkenes.

Alkene	Reaction	lg$A$*	E, kcal	Ref.
CHD=CHD	*cis* → *trans*	13.00	65.0	11
CHCl=CHCl	*trans* → *cis*	12.70	42.0	6
CHCl=CHCl	*trans* → *cis*	12.68	55.3	9
CHCl=CHCl	*cis* → *trans*	12.76	56.0	9
$CH_3CH=CHCH_3$	*cis* → *trans*	13.78	62.8	15
$CH_3CH=CHCH_3$	*cis* → *trans*	11.00	52.0	14
$CH_3CH=CHCH_3$	*cis* → *trans*	14.54	65.0	18
$CH_3CH=CHCH_3$	*cis* → *trans*	14.00	64.2	16
$CF_3CF=CFCF_3$	*cis* → *trans*	13.53	56.4	20
p-$CH_3OC_6H_4CH=CHC_6H_5$	*cis* → *trans*	10.23	35.5	22
p-NO_2—$C_6H_4CH=CHC_6H_5$	*cis* → *trans*	10.23	34.0	22
$C_6H_5CH=CHCOOCH_3$	*cis* → *trans*	10.54	41.6	21
$C_6H_5CH=CHCN$	*cis* → *trans*	11.60	46.0	23
$C_6H_5CH=CHCN$	*trans* → *cis*	11.80	46.0	23
$C_6H_5CH=CHC_6H_5$	*cis* → *trans*	12.78	42.8	24
$CH_3CH=CHCOOCH_3$	*cis* → *trans*	13.20	57.8	70
$CH_3CH=CHCN$	*cis* → *trans*	11.00	51.3	71

* Here and subsequently the units of A are s^{-1} and cm^3 $mole^{-1}$ s^{-1} for first-order and second-order reactions respectively.

However, careful analysis shows that the matter is complicated by several secondary factors, which throw doubt on the reliability of the results. It has recently become obvious that many *cis–trans* isomerisations, which have previously been regarded as unimolecular homogeneous reactions, are actually initiated by free radicals or are heterogeneous.

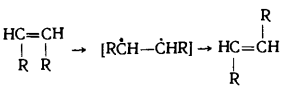
An example of such a reaction is the isomerisation of 1,2-dichloroethylene. In this case it was discovered[6] that, in order to obtain reproducible results, the reaction vessel had to be "aged", but even in an "old" vessel the reproducibility of the rate constant rarely became better than 50%.[7] A considerable departure from the first order was found[8] during the first 5 min of an experiment. The reaction velocity depends also on the surface–volume ratio S/V of the reaction vessel[9]. Finally, Steel[10] showed that the isomerisation of 1,2-dichloroethylene is strongly inhibited by toluene and propene, so that it is a radical-chain reaction. The isomerisation rate constant has been measured[9] in excess of toluene. This constant, when extrapolated to $S/V = 0$, is ascribed to a true unimolecular reaction, the activation energy then being 56 kcal.

The above complications explain the contradictions in published experimental results, and prevent an unambiguous conclusion from being drawn on the reaction mechanism.

A similar situation is found in the isomerisation of dideuterioethylene. The rate of this reaction depends[11] on the surface area of the reaction vessel, and increases on the addition of oxygen, ethanethiol, azomethane, and nitric oxide. The first-order rate constant increases with pressure over a wide range (9–312 mmHg). The activation energy at $p = \infty$ is 65 kcal. The isomerisation of dideuterioethylene in the presence of nitric oxide is of the first order with respect to the latter, and the activation energy is 27.5 kcal[12].

Many investigators have studied the *cis–trans* isomerisation of but-2-ene. In 1936 Kistiakowsky and Smith found[13] that the activation energy of this reaction had the unexpectedly low value of $E = 18$ kcal, which was difficult to explain. Later measurements by Anderson et al.[14], who used an improved method, gave a value of 52 kcal. In these experiments (over the pressure range 200–400 mmHg) some increase in pressure was observed during the reaction, probably caused by secondary reactions. Rabinovitch and Michel[15] found that, at pressures exceeding 10 mmHg, the reaction was complicated in character (autocatalytic) and sensitive to additions of oxygen, azomethane, and propene. Below this pressure, however, isomerisation was regarded[15] as unimolecular with an activation energy of 62.8 kcal. Other authors[16,17] have reached similar conclusions. The kinetics of the isomerisation of but-2-ene has been studied also at considerably higher temperatures in a shock tube[18]. On extrapolating the early results[16,17] to the conditions of their own experiments, these workers found[18] the activation energy to be 65 kcal.

Thus at present the mechanism of *cis–trans* isomerisations cannot be regarded as finally established. Complications due to the occurrence of heterogeneous reactions and the possible influence of free radicals, observed by several workers, compel a very cautious approach to the expressions obtained for the isomerisation rate constants. If recent results are correct, the activation energies of *cis–trans* isomerisations will be larger than those assumed earlier. These quantities are close to the mean energy of the π-C=C bond in alkenes, and it may therefore be supposed that isomerisation is accompanied by the formation of an unstable biradical intermediate:



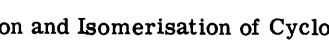
This possibility had been pointed out earlier by Kondrat'ev[19]. The intermediate biradical is in a singlet state, so that the reaction takes place without change in the multiplicity, as is indicated by the "normal" values of the pre-exponential factors.

With this reaction mechanism *cis–trans* isomerisation by definition is not a molecular reaction, and its consideration is in general outside the scope of the present review. Nevertheless, certain other reactions are discussed, where the mechanism is also a matter of controversy.

2. Decomposition and Isomerisation of Cyclobutanes

Two types of chemical changes—(1) decomposition into two alkene molecules and (2) *cis–trans* isomerisation—are possible in the case of cyclobutane derivatives.

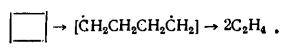
If the decomposition of cyclobutane is a single-stage unimolecular reaction, the structure of the corresponding activated complex can be represented



This involves the cleavage of two σ-C=C bonds in the four-membered ring, with the formation of two π-C=C bonds. The additive activation energy of this reaction is $E = 60 + 79 - (12 + 28 + 2 \times 17) = 65$ kcal, which agrees with most of the experimental results in Table 4.

However, we have tacitly assumed that activated π-bonds are not conjugated, and we have not introduced appropriate corrections. This can be justified by the fact that the decrease in energy of the system resulting from conjugation is to a considerable extent balanced by the increase due to the high deformation energy for the four-membered ring. Indeed, the deformation energy in cyclobutadiene, for example, is so large that this compound is probably absolutely unstable, and all attempts at its synthesis have failed.

A single-stage mechanism is supported by the fact that the rate of this reaction depends neither on the surface–volume ratio S/V nor on additions of inhibitors of radical reactions. Nevertheless, several workers assume that the decomposition of cyclobutanes takes place in two stages, with the intermediate formation of an unstable biradical:

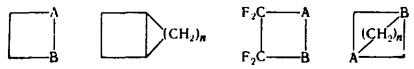


If the first stage is rate-determining, the activation energy should be equal to the energy of rupture of a carbon–carbon bond in cyclobutane, i.e. 60 kcal. This value is also close to experimental values of the activation energy.

It is therefore difficult to draw a final conclusion on the mechanism of the reaction. However, interesting work[25,26] on the decomposition and isomerisation of *cis-* and *trans-*1,2-dimethylcyclobutanes shows that, if an intermediate biradical is formed, its decomposition is more rapid than rotation about the carbon–carbon bond. Indeed, this work has revealed firstly that the rate of *cis–trans* isomerisation of cyclobutane is far lower than its rate of decomposition, although the activation energy of isomerisation is also rather smaller; and secondly that, in the decomposition of 1,2-dimethylcyclobutanes with the formation of but-2-ene and ethylene, non-equilibrium proportions of the *cis-* and *trans-*isomers are formed, the butene which corresponds in configuration to the original cyclobutane always being produced preferentially. These facts undoubtedly suggest that the lifetime of the hypothetical biradical is extremely short, probably shorter than the time of rotation about the carbon–carbon bond. Experimental data on the kinetics of the *cis–trans* isomerisation of cyclobutanes are listed in Table 5.

It is interesting also to note the appreciable differences in decomposition kinetics between cyclobutane and its derivatives containing a double bond in the β-position relative to the ring: the activation energy of decomposition of the latter is about 12 kcal smaller than that of cyclobutane.

Table 4. Kinetic data on the decomposition of cyclobutane and its derivatives (I)–(IV).



(I) (II) (III) (IV)

Compound type	A	B	n	Reaction products	lgA	E, kcal	Ref.
I	CH_2	CH_2	—	$2C_2H_4$	15.60	62.5	31
I	CH_2	$CHCH_3$	—	$C_2H_4+C_3H_6$	15.38	61.2	32
I	CH_2	$CHCH_3$	—	$C_2H_4+C_3H_6$	15.64	62.0	33
cis-I	$CHCH_3$	$CHCH_3$	—	$2C_3H_6$	15.48	60.4	25
cis-I	»	$CHCH_3$	—	$C_2H_4+CH_3CH=CHCH_3$	15.57	63.0	25
trans-I	$CHCH_3$	$CHCH_3$	—	$2C_3H_6$	15.45	61.6	26
trans-I	»	$CHCH_3$	—	$C_2H_4+CH_3CH=CHCH_3$	15.46	63.4	26
I	CH_2	CHC_2H_5	—	$C_2H_4+CH_2=CHC_2H_5$	15.56	62.0	34
I	CH_2	$CHCH(CH_3)_2$	—	$C_2H_4+CH_2=CHCH(CH_3)_2$	15.63	62.6	35
I	CH_2	CHC_3H_7-n	—	$C_2H_4+CH_2=CHC_3H_7$-n	15.53	61.6	36
I	CH_2	$CHC(CH_3)=CH_2$	—	$C_2H_4+CH_2=CHC(CH_3)=CH_2$	14.64	51.0	28
I	CH_2	$C=CH_2$	—	$C_2H_4+CH_2=C=CH_2$	15.68	63.3	40
I	CH_2	$C=CH_2$	—	$C_2H_4+CH_2=C=CH_2$	15.09	61.5	41
I	CH_2	$C=O$	—	$C_2H_4+CH_2=C=O$	14.56	52.0	23
I	CH_2	$CHCHO$	—	$C_2H_4+CH_2=CHCHO$	14.43	53.3	44
I	CH_2	$CHCOCH_3$	—	$C_2H_4+CH_2=CHCOCH_3$	14.53	54.5	45
I	CH_2	$CHCOC_2H_5$	—	$C_2H_4+CH_2=CHCOC_2H_5$	14.50	54.2	46
I	CH_2	$CHCOOCH_3$	—	$C_2H_4+CH_2=CHCOOCH_3$	14.84	57.3	47
II	—	—	2	$CH_2=CH(CH_2)_2CH=CH_2$	15.40	36.0	37
II	—	—	3	C_3H_4+ cyclo-C_5H_8	14.84	60.7	38
II	—	—	3	$CH_2=CH(CH_2)_3CH=CH_2$	15.40	64.0	38
III	CF_2	CF_2	—	$2C_3F_4$	16.00	73.3	48
III	CF_2	CF_2	—	$2C_2F_4$	15.95	74.1	49
		reverse reaction			10.40	24.0	48
		ditto			11.22	26.3	50
		»			11.01	25.4	51
cis-III	CFCl	CFCl		$2C_2F_3Cl$	15.50	69.3	52
trans-III	CFCl	CFCl		$2C_2F_3Cl$	15.09	65.3	52
		reverse reaction			10.63	26.6	52
	reaction	$C_2F_3+C_2F_4\rightarrow$III,	A=CF_2,	B=CFCl	10.93	26.3	50
cis-III	$CFCF_3$	$CFCF_3$		$2C_3F_6$	15.36	64.2	53
trans-III	$CFCF_3$	$CFCF_3$		$2C_3F_6$	15.77	64.2	53
IV	CH	CH	0	$CH_2=CHCH=CH_2$	14.02	40.58	56
IV	CCH_3	CCH_3	0	$CH_2=C(CH)_3C(CH_3)=CH_2$	14.45	43.3	42
IV	CH	CH	2	$CH_2=CH(CH_2)_2CH=CH_2$	15.17	55.0	54
					12.81	33.5	39
					15.51	55.9	55

Table 5. Kinetic data on the *cis–trans* isomerisation of the cyclobutane derivatives (I) and (III)*.

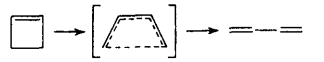
Compound	Reaction	lg A	E, kcal	Ref.
I, A=B=$CHCH_3$	*cis* → *trans*	14.81	60.1	25
ditto	*trans* → *cis*	14.57	61.3	26
III, A=B=$CFCF_3$	*cis* → *trans*	15.36	64.2	53
ditto	*trans* → *cis*	15.77	64.2	53
III, A=B=CFCl	*trans* → *cis*	15.10	60.1	52
ditto	*cis* → *trans*	14.86	60.2	52

* See Table 4.

With a biradical mechanism this decrease in the activation energy of decomposition is attributed to the resonance (stabilisation) energy of an allylic radical $\cdot CH_2CH_2CH_2\dot{C}HCH:CH_2$.[27,28] However, this energy is considerably smaller than for allyl itself $CH_2:CH.CH_2\cdot$, where it is 22 kcal‡.

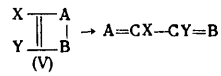
3. Isomerisation of Cyclobutenes

The isomerisation of cyclobutene and its derivatives into dienes has been studied in detail by Frey and Walters[56–65]. These are first-order reactions, and their rate is affected neither by change in the surface–volume ratio nor by additions of inhibitors. The view that these are true unimolecular reactions is entirely justified. Isomerisation involves the cleavage of one C–C bond in the four-membered ring and one π-bond, while three (activated) cumulative π-bonds and one σ-bond are formed:

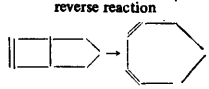
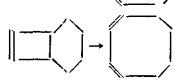
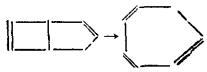


The additive activation energy of this reaction is $E = 60 + 61 - (12 + 3 \times 17 + 3 \times 8) = 34$ kcal.

Table 6. Kinetic data on the isomerisation of cyclobutenes (V).



(V)

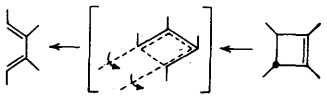
X	Y	A	B	lgA	E, kcal	Ref.
H	H	CH_2	CH_2	13.08	32.5	57
—	—	—	—	13.26	32.7	58
CH_3	H	CH_2	CH_2	13.79	35.1	59
CH_3	CH_3	CH_2	CH_2	13.84	36.04	60
CH_3	H	CH_2	$CHCH_3$	13.65	33.0	61
CH_3	H	$CHCH_3$	CH_2	13.52	33.39	61
H	H	CH_2	$C(CH_3)_2$	13.93	36.09	62
CH_3	H	CH_2	$C(CH_3)_2$	13.90	37.03	62
H	H	$CHCH_3$	CH_2	13.53	31.55	63
H	C_2H_5	CH_2	CH_2	13.76	34.83	65
CH_3	CH_3	$CHCH_3$	$CHCH_3$	13.85 (*trans*-)	33.59 (*trans*-)	64
—	—	—	—	14.10 (*cis*-)	37.36 (*cis*-)	64
F	F	CF_2	CF_2	14.12	47.08	66
		reverse reaction		12.03	35.38	66
				14.31	45.51	67
				14.13	43.18	64
				14.00	39.5	69

This value shows excellent agreement with available experimental data (Table 6), except for the reactions of dicyclic compounds and perfluorocyclobutene, the activation energies of which are 10–13 kcal higher. In the case perfluorocyclobutene the presence of fluorine atoms probably greatly affects the energies of the bonds in the molecule. Such deviation from a simple additive scheme is a

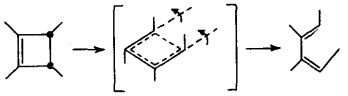
‡ The stabilisation energy of a radical can be estimated as the difference between the mean energy and the energy of rupture of a carbon–hydrogen bond in the molecule[29]. For propene this will give[30] $E_{stab} = 99 - 77 = 22$ kcal.

general phenomenon in the reactions of perfluorinated compounds, which requires the introduction of appropriate corrections into the scheme.

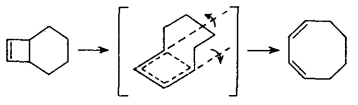
Special interest attaches to the isomerisation of dicyclic compounds, where the departure from additivity is due to the peculiar stereochemistry of the process. In fact the isomerisation of substituted cyclobutenes involves rotation of the terminal groups formed, where "unidirectional" rotation (the *conrotatory* process) is energetically more favourable. Thus, *trans*-1,2,3,4-tetramethylcyclobutene yields 3,4-dimethylhexa-*trans*-2,*trans*-4-diene:



whereas, *cis*-1,2,3,4-tetramethylcyclobutene gives 3,4-dimethylhexa-*cis*-2,*trans*-4-diene[64]:



In dicyclic molecules, however, such unidirectional rotation is impossible, and isomerisation is accompanied by rotation in the opposite direction (*disrotatory* process)[64]:



Since "opposite" rotation is energetically less favourable, the activation energy is appreciably higher in these cases.

There is a qualitative quantum-mechanical explanation of these peculiarities in terms of the symmetry of the molecular orbitals of the electrons taking part in the reaction[68]. In a conrotatory process two σ-electrons and two π-electrons of the initial molecule pass into the two lowest orbitals ψ_1 and ψ_2 of the resulting butadiene:

$$\sigma^2\pi^2 \rightarrow \psi_1^2\psi_2^2.$$

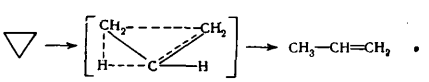
With a disrotatory process two of these electrons should pass into a higher level ψ_3 in order to maintain the symmetry of the orbitals:

$$\sigma^2\pi^2 \rightarrow \psi_1^2\psi_3^2 \ .$$

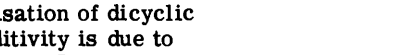
Thus the departure from additivity in the isomerisation of dicyclic molecules finds a simple explanation in the method of molecular orbitals.

4. Isomerisation of Cyclopropanes

Two types of isomerisation—structural isomerisation with the formation of alkenes and geometrical *cis–trans* isomerisation—occur in cyclopropane and its derivatives, as also in cyclobutane. A theoretical treatment of and kinetic data on the structural isomerisation of cyclopropanes into alkenes will be found in several papers[72-92,202]. Two mechanisms have been suggested for this reaction. Smith[72] suggested that isomerisation involves formation of a transition state containing five atoms in the same plane:



An alternative mechanism, with intermediate formation of the short-lived biradical trimethylene, was put forward by Rabinovitch et al.[73]:



Additive calculation of the activation energy of isomerisation and also several other arguments[74,81] tip the balance in favour of the biradical mechanism of isomerisation. In fact the calculated activation energy for the first mechanism $E = 50 + 99 - (4 + 2 \times 45 + 17) = 38$ kcal differs markedly from the experimental value of 65 kcal. This implies that the reaction does not take place by the first mechanism.

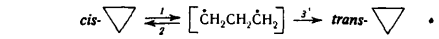
The scheme proposed by Rabinovitch for the alternative biradical mechanism must be supplemented by reaction *2*, the reverse reaction to formation of the trimethylene radical[75]:

The isomerisation rate constant for this extended mechanism is $k = k_1k_3/(k_2 + k_3)$, where k_1, k_2, and k_3 are the rate constants of the corresponding reactions. When $k_3 \ll k_2$, we have $k \simeq k_3k_1/k_2 = k_3K_{eq}$, where K_{eq} is the equilibrium constant for the formation of trimethylene from cyclopropane. According to Benson[75]

$$k_1 = 10^{16.0}\exp(-64200/RT)$$
$$k_2 = 10^{13.0}\exp(-8200/RT)$$
$$k_3 = 10^{13.2}\exp(-9500/RT) \ .$$

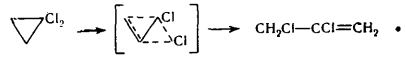
The expression for k_1 was obtained on the assumption that the rate of reaction *1* was equal to the rate of geometrical isomerisation of cyclopropane.

Rabinovitch and his coworkers found[73] that the rate of geometrical isomerisation of dideuteriocyclopropane exceeded its rate of structural isomerisation about sixteenfold. This is perfectly understandable when it is remembered that the intermediate trimethylene biradical is common to the two reactions:



Comparison of data on the kinetics of the geometrical isomerisation of cyclopropanes (Table 8) with those on the structural isomerisation of the same compounds (Table 7) shows that the activation energy of *cis–trans* isomerisation is the lower. This is due to the lower potential barrier to internal rotation in the biradical than to its isomerisation into propene. Hence in this case $k_3' \gg k_2$ and $k_{geom} = k_1k_3'/(k_2 + k_3') \simeq k_1$, in agreement with Benson's conclusions[75].

It is interesting that 1,1-dichlorocyclopropane isomerises into 2,3-dichloropropene with migration of a chlorine atom, not of a hydrogen atom[76]:



From the experimental results the authors[76] conclude that this reaction has a single-stage mechanism with an activation energy of 57.8 kcal, which agrees with the additive value of 55 kcal.

5. Isomerisation of Vinylcyclopropanes

A peculiar type of isomerisation with expansion of the ring is observed with compounds containing a C=C double bond in the β-position to the ring. The simplest compound

of this type is vinylcyclopropane, which isomerises into cyclopentene:

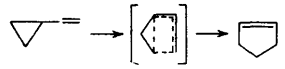
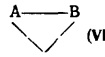
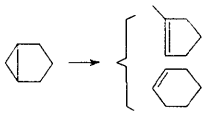
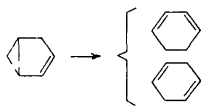
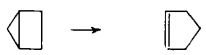


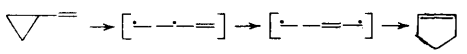
Table 7. Kinetic data on the structural isomerisation of cyclopropanes (VI).



VI A	VI B	Reaction products	lg A	E, kcal	Ref.
CH_2	CH_2	C_3H_6	15.30	65.1	77
			15.17	65.0	78
			14.84	64.2	79
			15.85	67.2	203
			15.26	65.9	204
CH_2	$CHCH_3$	C_4H_8	15.45	65.0	80
			14.46	63.2	81
CH_2	$C(CH_3)_2$	C_5H_{10}	15.05	62.6	82
$CHCH_3$ (*cis*)	$CHCH_3$ (*cis*)	*cis*-$CH_3CH{=}CHC_2H_5$	14.05	61.8	83
			13.92	61.4	84
		trans-$CH_3CH{=}CHC_2H_5$	14.13	61.8	83
			13.96	61.2	84
		$(CH_3)_2C{=}CHCH_3$	13.28	59.7	83
			14.08	62.3	84
		$CH_2{=}C(CH_3)C_2H_5$	13.21	59.6	83
			13.93	61.9	84
$CHCH_3$ (*trans*)	$CHCH_3$ (*trans*)	*cis*-$CH_3CH{=}CHC_2H_5$ *trans*-$CH_3CH{=}CHC_2H_5$	14.40	63.6	84
			14.30	62.9	84
$C(CH_3)_2$	$C(CH_3)_2$	$(CH_3)_2CHCH{=}C(CH_3)_2$	15.83	64.4	85
CHC_2H_5	CHC_2H_5	$CH_2{=}CHCH(C_2H_5)_2$	14.95	63.8	86
		$CH_3CH{=}C(C_2H_5)_2$	14.84	63.4	86
CH_2	$CHCH{=}C(CH_3)_2$	$CH_2{=}CHCH_2CH{=}C(CH_3)_2$	14.61	56.65	87
		cis-$(CH_3)_2CH{=}CHCH{=}CHCH_3$	13.33	53.0	87
		trans-$(CH_3)_2C{=}CHCH{=}CHCH_3$	13.25	52.1	87
CH_2	CHF	C_3H_5F	14.58	61.01	88
CH_2	$CHCl$	$CH_2ClCH{=}CH_2$	14.8	56.2	92
CH_2	CCl_2	$CH_2ClCCl{=}CH_2$	15.13	57.8	76
CHD	CHD	$C_3H_4D_2$	15.20	65.5	73
			15.12	65.4	204
CH_2	$CHCF_3$	$C_3H_5CF_3$	14.60	65.6	205
CH_2	$CHCH_2CF_3$	$C_4H_7CF_3$	14.38	63.6	205
			13.89	61.17	89
			13.29	57.4	89
			14.28	50.2	90
			14.09	50.2	90
			14.58	46.6	91

This reaction involves the cleavage of one π-bond and one σ-C–C bond in the three-membered ring. The additive activation energy of this reaction is $E = 50 + 61 - (4 + 17 + 17 + 22) = 51$ kcal.

Two mechanisms have been suggested for reactions of this type—via a four-membered activated complex, as indicated above[95], and a biradical mechanism involving the formation and isomerisation of a biradical[96]



The first mechanism is supported by two arguments: firstly the pre-exponential factor in these reactions is smaller by $10^{1.5-2}$ than in the isomerisation of cyclopropanes into alkenes, which involves the intermediate formation of biradicals (see subsection 4); secondly, the activation energy of the isomerisation of vinylcyclopropane into pentadienes, which has a biradical mechanism, exceeds that for the present reaction by 6–7 kcal (see Table 7).

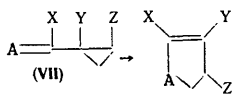
Table 8. Kinetic data on the geometric isomerisation of cyclopropanes (VI). *cis*-VI → *trans*-VI

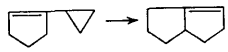
VI A	VI B	lg A	E, kcal	Ref.
CHD	CHD	16.00	64.2	73
$CHCH_3$	$CHCH_3$	15.25	59.4	83
CHC_2H_5	$CHCH_3$	15.08	58.9	93
1,2,3-trimethylcyclopropane		15.78	60.9	94

Available experimental data (Table 9) show excellent agreement with the additive activation energy, which suggests that the reaction takes place by the first mechanism.

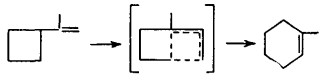
It is interesting that the activation energy of the isomerisation of perfluorovinylcyclopropane is considerably smaller because of the greater deformation energy of this compound compared with cyclopropane. It has been estimated[103] as $\Delta Q_{def} = 43–50$ kcal, compared with ~ 28 kcal in the case of cyclopropane[155].

Table 9. Kinetic data on the isomerisation of vinylcyclopropanes (VII).



VII A	X	Y	Z	lg A	E, kcal	Ref.
CH_2	H	H	H	13.61	49.7	97
$C(CH_3)_2$	H	H	H	13.50	49.6	98
CH_2	CH_3	CH_3	H	14.40	54.6	87
CH_2	H	CH_3	H	14.14	50.2	99
CH_2	CH_3	H	H	14.11	49.35	100
CHC_2H_5	H	H	H	13.89	50.9	96
CH_2	H	H	CH_3 (*trans*)	13.79	49.88	95
				13.67	48.64	101
CH_2	cyclo-C_3H_5	H	H	14.29	51.06	102
perfluorovinylcyclopropane C_5F_8				13.895	34.6	103
				14.01	51.29	102

Substituted cyclobutanes undergo analogous isomerisation with an activation energy of 51 kcal[28]:



6. Decomposition of Esters

Esters containing a carbon atom in the β-position relative to the carboxyl decompose into an acid and an alkene:

$$RCOOR' \rightarrow RCOOH + \text{Alkene}\ .$$

The activated complex of this reaction is either four-membered or six-membered:

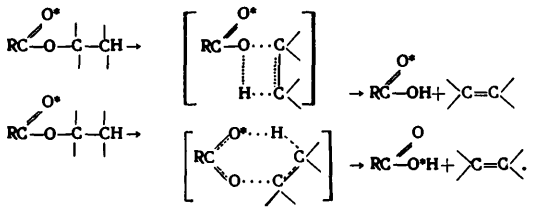


Table 10. Kinetic data on the decomposition of esters.

$$R^1-C(=O)-OR \rightarrow R^1-C(=O)-OH + >C=C<$$

R	R′	Alkene	lgA	E, kcal	Ref.
C_2H_5	H	C_2H_4	11.33	44.1	104
			11.57	44.03	105
C_2H_5	CH_3	C_2H_4	12.49	47.8	104
C_2H_5	C_2H_5	C_2H_4	12.72	48.5	106
iso-C_3H_7	H	C_2H_4	12.33	44.2	104
iso-C_3H_7	CH_3	C_2H_4	13.00	45.0	104
			12.88	44.8	206
t-C_4H_9	H	iso-C_4H_8	11.10	34.0	107
t-C_4H_9	CH_3	iso-C_4H_8	13.34	40.5	108
t-C_4H_9	C_2H_5	iso-C_4H_8	12.80	39.2	108
$C_2H_5C(CH_3)_2$	CH_3	C_5H_{10}	13.50	40.1	109
$C_6H_5CHCH_3$	CH_3	$CH_3CH=CHCH_3$	13.12	46.6	110
$CH_2=CHCH_2CHCH_3$	CH_3	$CH_2=CHCH=CHCH_3$ + $+CH_2=CHCH_2CH=CH_2$	13.00	44.4	111
$CH_3COCH_2CHCH_3$	CH_3	$CH_3COCH=CHCH_3$	11.88	37.4	111
$C_6H_5CH_2CHC_6H_5$	CH_3	$C_6H_5CH_2CH=CHC_6H_5$	13.05	43.3	112
$CH_3CHC_6H_5$	CH_3	$C_6H_5CH=CH_2$	12.81	43.7	115
C_2H_5	$(CH_3)_2C$	C_2H_4	11.24	44.0	114
$C_{27}H_{45}$ (cholesteryl)	CH_3	$C_{27}H_{44}$	12.71	44.1	113

Table 11. Kinetic data[197] on the decomposition of acetates.

$$X-C_6H_4CHCH_2C_6H_4-Y \rightarrow X-C_6H_4CH=CHC_6H_4-Y + CH_3COOH$$
$$\quad\quad\quad

8. Decomposition of Alkyl Halides

A large number of investigations have been made on the mechanism and the kinetics of the thermal decomposition of alkyl halides to form an alkene and a hydrogen halide. The study of reactions of this type is complicated by the fact that, depending on their structure, alkyl halides may decompose either by a molecular or by a chain mechanism. Summarising a large amount of experimental information, Semenov[29] concluded that a molecular mechanism of decomposition was undergone only by those alkyl halides which, having lost a hydrogen atom, were incapable, because of the peculiar structure of the molecule, of forming an alkene by elimination of the halogen atom. Furthermore, the decomposition of alkyl halides is extraordinarily sensitive to the condition of the surface of the reaction vessel[29].

Experimental determination of the rate constants of unimolecular decomposition in particular is therefore difficult. Szwarc[116] used a toluene method to determine the unimolecular decomposition constants of an alkyl bromide, on the assumption that the presence of toluene suppresses radical side-reactions. To eliminate the effect of heterogeneous reactions on the kinetics of the unimolecular decomposition of ethyl chloride, we have studied[5] the reaction kinetics in a stream of an inert gas. Comparison of the rate of decomposition under these conditions with the rate on the packing in a column also enabled the rate constant of the heterogeneous reaction to be determined.

In spite of the above difficulties, a large number of rate constants have now been determined for the elementary reactions in the decomposition of alkyl halides. In all reactions of this type a four-membered activated complex is formed:

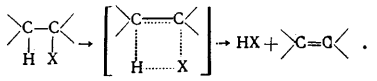


Table 13. Activation energy for the decomposition of alkyl halides (calculated). RX → HX + Alkene

Alkyl	X		
	Cl	Br	I
Primary	55	51	53
Secondary	48	46	45
Tertiary	41	41	37

Analysis of existing experimental results shows that the activation energy of these reactions is appreciably dependent on whether the halogen atom X is attached to a primary, secondary, or tertiary carbon atom. The activation energy for the decomposition of primary alkyl halides is rather higher (5–8 kcal) than for the secondary compounds, and the values for the latter are higher than for tertiary alkyl halides.

In the additive calculation of activation energy this is allowed for by the different mean energies of the activated bonds $C_{prim}...X$, $C_{sec}...X$, and $C_{tert}...X$. The influence of the immediate environment of the carbon atom on the energy of the activated bond C...X is exhibited here quite clearly. This effect is observed only with halogen atoms, and is probably caused by their great electronegativity, as a consequence of which the activated bond is strongly polar in character, approaching an ionic bond in polarity.

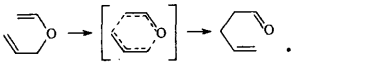
The additive activation energy for the decomposition of alkyl halides can be represented by the formula

$$E = 99 + Q_{C-X} - (45 + 17 + Q^{*}_{H-X} + Q^{*}_{C-X}) = 37 + Q_{C-X} - Q^{*}_{H-X} - Q^{*}_{C-X}.$$

Calculated activation energies for the decomposition of primary, secondary, and tertiary alkyl halides are listed in Table 13. Comparison with the numerous experimental values available (Table 14) shows good agreement with the calculated additive values.

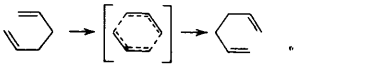
9. Claisen and Cope Rearrangements

Intramolecular rearrangements accompanied by inversion of an allyl group are widely known in organic chemistry. In the case of ethers such reactions are termed Claisen rearrangements. The reaction can be represented by the scheme



(1)

The Cope rearrangement can be represented by a similar scheme. The only difference is that here we have a carbon atom instead of the oxygen atom:



(1′)

The additive activation energies are—for the Claisen rearrangement

$$E = 2 \cdot 61 + 80 - (3 \cdot 17 + 18 + 27 + 28 + 4 \cdot 12) = 30 \text{ kcal}$$

and for the Cope rearrangement

$$E = 2 \cdot 61 + 79 - (4 \cdot 17 + 2 \cdot 28 + 4 \cdot 12) = 29 \text{ kcal}.$$

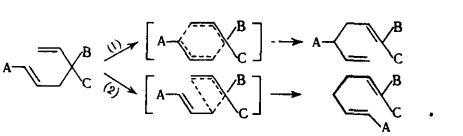
These values agree excellently with available experimental data (Table 15).

In the case of these rearrangements the experimental evidence for the structure of the activated complex, i.e. for the reaction mechanism, is quite complicated, and indeed a six-membered structure for the cyclic transition state has been confirmed only in isolated cases. Sometimes, however, the possibility is admitted[74] that a four-membered activated complex can be formed:

(2)

for the Cope rearrangement. A completely analogous scheme applies to the Claisen rearrangement.

To choose between these two mechanisms it is necessary to use a compound containing substituents attached both to the extreme carbon atom in the molecule (at position 6) and at position 3. Only in this case do reactions (1) and (2) yield products differing in structure:



The additive calculation of activation energy provides new opportunities for establishing the mechanism of a reaction. In the present case the activation energies calculated for six-membered and four-membered activated complexes differ markedly. For reaction (2), for example, the activation energy is $E = 79 + 61 - (2 \times 17 + 2 \times 28) = 50$ kcal.

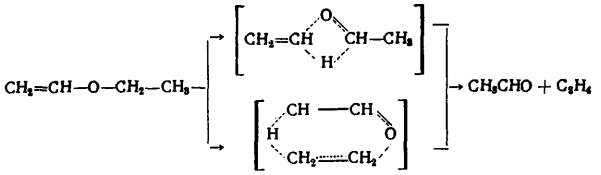
Table 14. Kinetic data on the decomposition of alkyl halides. R–X → HX + Alkene

Alkyl halide RX	lgA	E, kcal	Ref.
Ethyl chloride	13.16	56.46	117
	13.46	56.62	118
	13.45	55.00	119
	14.03	58.43	120
1-Chloropropane	13.50	55.08	121
	13.45	55.00	119
1-Chlorobutane	13.63	55.15	121
	14.00	57.00	119
1-Chloropentane	13.81	55.33	121
	14.61	58.3	122
1,6-Dichlorohexane	14.50	58.00	123
1-Chlorododecane	14.10	55.7	123
1,10-Dichlorodecane	13.35	53.0	123
2-Chloropropane	13.40	50.5	124
	13.64	51.1	117
2-Chlorobutane	13.62	49.6	126
	14.07	50.75	127
	13.75	50.1	128
3-Chloropentane	12.29	45.0	123
4-Chlorododecane	11.95	43.4	123
1,2-Dichlorohexane	13.42	50.0	123
2,5-Dichlorohexane	12.63	46.2	123
2,2-Dichloroheptane	12.80	45.0	123
5,7-Dichlorododecane	14.25	49.5	123
6,7-Dichlorododecane	13.60	49.3	123
Chlorocyclopentane	13.47	48.3	129
Chlorocyclohexane	13.50	49.2	129
2-Chloro-2-methylpropane	12.40	41.4	130
	13.73	45.0	131
	13.90	46.2	132
2-Chloro-2-methylbutane	13.82	44.2	131
2-Chloro-2,3-dimethylbutane	13.38	42.3	131
3-Chloro-3-methylheptane	12.38	38.0	123
3-Chloro-3-methylundecane	11.30	36.0	123
2-Chlorohept-1-ene	13.55	55.0	123
4-Chlorohept-3-ene	14.00	57.0	123
4-Chlorohex-2-ene	10.75	34.0	123
Ethyl bromide	13.19	53.7	117
	12.86	52.3	133
	13.25	53.7	150
	13.45	53.9	135
1-Bromopropane	12.90	50.7	140
	13.00	50.7	133
1-Bromobutane	13.18	50.9	140
1-Bromopentane	13.09	50.5	137
1-Bromohexane	13.13	50.5	137
1-Bromo-2-methylpropane	13.05	50.4	138
3-Bromopropene	12.33	45.5	139
2-Bromopropane	13.62	47.8	117
	12.60	47.7	133
	12.74	47.0	136
2-Bromobutane	12.63	43.8	141
	13.04	45.5	142
	13.53	46.5	134
3-Bromopentane	13.51	45.44	143
Bromocyclopentane	11.90	41.4	125
	12.84	43.7	145
Bromocyclohexane	13.51	46.1	146
4-Bromopent-1-ene	12.94	44.7	135
2-Bromo-2-methylpropane	13.50	41.5	132
	14.00	42.0	147
	13.23	41.0	142
2-Bromo-2-methylbutane	13.60	40.5	148
Ethyl iodide	13.36	50.0	149
	14.80	53.7	150
2-Iodopropane	14.49	48.0	154
	13.20	42.9	151
	13.67	45.1	117
	14.46	48.2	155
	12.96	43.5	152
2-Iodobutane	14.90	47.9	154
2-Iodo-2-methylpropane	12.52	36.4	153
	13.73	38.1	117

The analogous calculation for the Claisen rearrangement via a four-membered complex gives 51 kcal. These values differ by more than 20 kcal from the experimental values of the activation energy. The agreement with experiment of activation energies calculated for the six-membered complex, and the sharp divergence between the corresponding values for the four-membered complex, show quite obviously that the reaction takes place by the first mechanism.

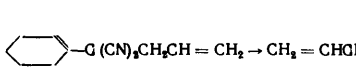
10. Decomposition of Unsaturated Ethers

Several unsaturated ethers decompose with the formation of alkenes and aldehydes. For example, ethyl vinyl ether when heated breaks down into acetaldehyde and ethylene. Two possible mechanisms—



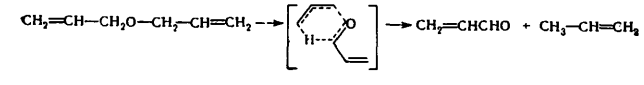
have been suggested and discussed[161,162] for this reaction. Additive calculation of the activation energy for the first mechanism, involving formation of a four-membered activated complex, gives $E = 80 + 99 - (18 + 27 + 2 \times 45) = 44$ kcal. For the second route, with formation of a six-membered activated complex, $E = 90 + 80 + 61 - (2 \times 45 + 18 + 27 + 2 \times 17 + 2 \times 12) = 47$ kcal.

Table 15. Kinetic data on allylic rearrangements.

Reaction	lgA	E, kcal	Ref.
$CH_2=CHCH_2CH_2CH=CHCH_3 \rightarrow CH_2=CHCH_2CHCH=CH_2$ (CH₃)	9.09	32.5	144
$CH_2=CHCH_2CHCH=CH_2 \rightarrow CH_2=CHCH_2CH_2CH=CHCH_3$ (CH₃)	9.84	32.5	144
$CH_2=CHCH_2C(CN)_2C=CHCH_3 \rightarrow CH_2=CHCH_2CHC=C(CN)_2$ (C₂H₅; CH₃, C₂H₅)	10.94	25.78	157
$CH_2=CHCH_2C(CO_2C_2H_5)C=CH-CH(CH_3)_2 \rightarrow CH_2=CHCH_2CHC(CH_3)=CCO_2C_2H_5$ (CN; CH₃; CH(CH₃)₂; CN)	10.36	28.62	157
	10.80	26.16	157
$CH_2=CHCH_2CH_2CH=C=CH_2 \rightarrow CH_2=CHCH_2C(=CH_2)-CH=CH_2$	9.93	28.47	158
$CH_2=CHCH_2OCH=CH_2 \rightarrow CH_3=CHCH_2CH_2CHO$	11.70	30.6	159
$CH_2=CHCH_2OC=CH_2 \rightarrow CH_2=CHCH_2CH_2COCH_3$ (CH₂)	11.37	29.3	160

Activation energies calculated for both mechanisms agree with the experimental values $E_{exp} = 42.3$–48.5 kcal (Table 16). However, analysis of the entropies of activation shows that the reaction involves formation of a six-membered complex[161]. There is also a direct experimental confirmation of this conclusion: the decomposition of isopropyl vinyl ether yields acetaldehyde and propene[163], whereas reaction involving a four-membered complex should have given ethylene and acetone.

A peculiar mechanism is observed in the decomposition of diallyl ether to form propene and acrylaldehyde[165]:



The activated complex in this case differs from the preceding one only in the relative position of the activated

bonds: therefore the calculated activation energy is also 47 kcal, which agrees satisfactorily[165] with the experimental value of 42.3 kcal.

11. Diels–Alder Reactions

Reactions of this type, which are termed also diene syntheses, are extremely important in organic chemistry and are widely used in the synthesis of various organic compounds. According to present-day ideas Diels–Alder reactions take place in a single act involving a six-membered activated complex:

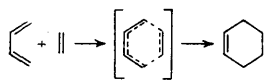
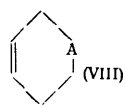


Table 16. Kinetic data on the decomposition of unsaturated ethers.

Reaction	lg A	E, kcal	Ref.
$CH_2=CHOC_2H_5 \rightarrow CH_3CHO + C_2H_4$	11.43 11.60	43.8 44.4	161 162
$CH_2=CHO\text{-iso-}C_3H_7 \rightarrow CH_3CHO + C_3H_6$	12.58	43.6	163
$CH_2=CHO\text{-n-}C_4H_9 \rightarrow CH_3CHO + C_4H_8$	11.15	42.38	164
$CH_2=CHCH_2OCH_2CH=CH_2 \rightarrow CH_2=CHCHO + C_3H_6$	11.95	42.3	165
$CH_2=CHCH_2OC_2H_5 \rightarrow CH_3CHO + C_3H_6$	12.89	48.5	165

Table 17. Kinetic data on Diels–Alder reactions.



(VIII)

Initial compounds	Reaction products	lgA	E, kcal	Ref.
$2CH_2=CHCH=CH_2$	VIII, $A=CHCH=CH_2$	11.14 9.96	26.8 23.7	166 167
VIII, $A=CHCH=CH_2$	$2CH_2=CHCH=CH_2$	15.20 15.70	62.0 61.8	168 169
$CH_2=CHCH=CH_2+C_2H_4$	VIII, $A=CH_2$	10.48	27.5	166
VIII, $A=CH_2$	$CH_2=CHCH=CH_2+C_2H_4$	15.02 15.16	66.7 66.2	168 170
$2CH_2=C(CH_3)CH=CH_2$ *	dimer	11.73 10.90	28.9 24.9	171 172
$2CH_2=CHCH=CHCH_3$	dimer	10.19	26.0	173
VIII, $A=CHCH_3$	$CH_2=CHCH=CH_2+CH_2=CHCH_3$	15.13	66.6	168
2 cyclo-C_5H_6 **	dimer	5.0—7.1	14.7—17.4	174

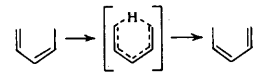
* Reaction in the liquid phase.
** Data on the kinetics of the reaction in various solvents.

All six π-electrons of the initial system are involved in the reaction. The activated complex contains four activated π-C=C bonds and two σ-C–C bonds. Three of the activated π-bonds form a cumulative chain, while one π-bond is conjugated.

Additive calculation gives a value for the activation energy of $E = 3 \times 61 - (4 \times 17 + 2 \times 28 + 3 \times 8 + 12) =$ 23 kcal, which agrees well with experimental data (Table 17). Rather larger deviations are observed with reactions in which dicyclic compounds are formed. In this case the additivity of the mean bond energies in the molecules probably breaks down.

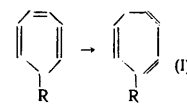
12. Diene Rearrangements

Dienes undergo an interesting type of reaction, accompanied by migration of a hydrogen atom:

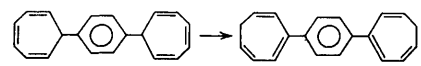


The additive activation energy of this process is $E = 2 \times 61 + 99 - (2 \times 45 + 4 \times 17 + 4 \times 8) = 31$ kcal. Here the activated complex contains two activated C–H bonds and a chain of four cumulative π-bonds. Thus the cumulation of four π-bonds must be taken into account in this case. The calculated activation energy agrees excellently with existing experimental data (Table 18).

Table 18. Kinetic data on diene rearrangements.

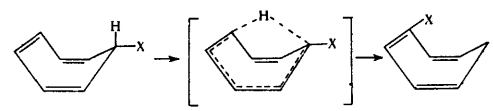


(I)

Reaction	lgA	E, kcal	Ref.
$CH_2=CHCH=CHC_2H_5 \rightarrow CH_3CH=CHCH=CHCH_3$	10.80	32.5	175
$CH_2=CCH_3CH=CHCH_3 \rightarrow CH_3CCH_3=CHCH=CH_2$	11.24	32.76	176
I, R=D	11.2	31.5	177
I, R=CH_3	12.60	33.3	178
I, R=OR′	10.04	26.4	179
I, R=C_6H_5 *	10.08	27.6	180
Cyclo-octa-1,3,6-triene → cyclo-octa-1,3,5-triene	11.74	28.9	182
$CHD_2CH=CHCH=CHD \rightarrow CD_2=CHCH=CHCH_2D$	11.45	36.3	183
	12.5	30.6	181

* Reaction in the liquid phase.

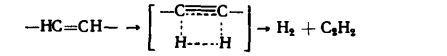
A particular type of diene rearrangement, which, however, has been most thoroughly studied, is the isomerisation of substituted cycloheptatrienes:



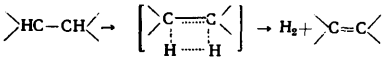
Although the structure of cycloheptatrienes differs from that of normal alkadienes, the activation energies of isomerisation are similar in the two cases. This fact yet again supports the concept underlying the additivity principle, that the energy of the transition state is determined solely by the activated bonds, while the presence of other chemical bonds, not altering in the activated complex and not involved in the reaction, has no effect on the activation energy within the limits of accuracy of the additive calculation.

13. Dehydrogenation

In most cases the dehydrogenation of molecules takes place by a chain mechanism. A classic example is the decomposition of ethane into ethylene and hydrogen. The mechanism of the dehydrogenation of ethylene with the formation of acetylene is a matter of controversy: some papers[184] assume a molecular mechanism, and others[185] a chain mechanism. The spread of experimental values for the activation energy of this reaction—from 20[186] to 86[187] kcal—is extremely wide. For the molecular mechanism

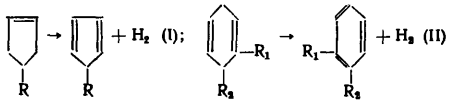


the additive activation energy is $E = 2 \times 99 - (2 \times 45 + 48 + 9) = 51$ kcal. According to the additive principle the dehydrogenation of alkanes to alkenes



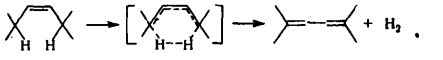
should be characterised by a lower activation energy $E = 2 \times 99 - (2 \times 45 + 48 + 17) = 43$ kcal, which agrees e.g. with data on the dehydrogenation of cyclopentane ($E_{exp} = 44$ kcal[188]).

Table 19. Kinetic data on the dehydrogenations (I) and (II).



Reaction	lgA	E, kcal	Ref.
I, R=H	13.34 13.01	59.9 58.8	189 190
I, R=O	12.72	48.5	191
II, $R_1=R_2=H$	12.36 12.02	43.8 42.7	192 90
II, $R_1=CH_3$; $R_2=H$	12.69	44.7	193
II, $R_1=H$; $R_2=CH_3$	12.47	42.95	194

Several studies have been made of the dehydrogenation of cycloalkenes, where hydrogen atoms are detached not from neighbouring carbon atoms but from those in the β-position with respect to the double bond:

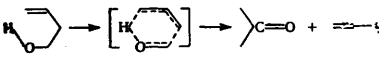


Reactions of this type are probably molecular.

Additive calculation gives for the activation energy $E = 2 \times 99 + 61 - (2 \times 45 + 48 + 3 \times 17 + 3 \times 8) = 46$ kcal, which agrees well with existing experimental results (Table 19). The data on the dehydrogenation of cyclopentene constitute an exception, and it is possible that in this case the reaction occurs partly by a chain mechanism.

14. Decomposition of Unsaturated Alcohols

In concluding this survey of experimental data let us consider the decomposition of an unsaturated alcohol into an alkene and an aldehyde or a ketone. Such decomposition has been most thoroughly studied with alcohols whose hydroxyl is in the γ-position relative to the double bond. The reaction is assumed to involve the formation of a six-membered activated complex:

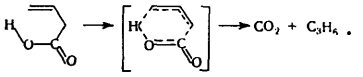


The activation energy calculated for this mechanism $E = 105 + 79 + 61 - (55 + 45 + 2 \times 17 + 28 + 18 + 2 \times 12) = 41$ kcal agrees excellently with existing experimental data (Table 20).

Table 20. Kinetic data on the decomposition of unsaturated alcohols.

Reaction	lgA	E, kcal	Ref.
$CH_2=CH(CH_2)_2OH \rightarrow H_2CO + C_2H_6$	11.65	41.0	195
$CH_2=CHCH_2CH(CH_2)OH \rightarrow CH_2CHO + C_2H_6$	11.93	40.8	195
$CH_2=CHCH_2C(CH_3)_2OH \rightarrow CH_2COCH_3 + C_2H_6$	12.14	40.7	195
$CH_2=C(C_6H_5)(CH_2)_2OH \rightarrow CH_2C(C_6H_5)=CH_2 + H_2CO$	11.80	38.9	195
$C_6H_5CH=CH(CH_2)_2OH \rightarrow C_6H_5CH_2CH=CH_2 + H_2CO$	11.58	42.8	195
$C_6H_5CH=CHCH_2C(C_2H_5)_2OH \rightarrow C_6H_5CH_2CH=CH_2 + (C_2H_5)_2CO$	12.04 12.14	41.75 41.8	196 195

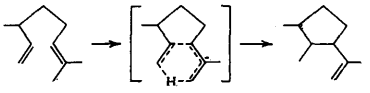
It is interesting that but-3-enoic acid decomposes by an analogous mechanism to form propene and carbon dioxide:



In this case, too, the experimental activation energy $E_{exp} = 39.3$ kcal[197] is close to the calculated value.

V. EFFECT OF CONJUGATED AND CUMULATIVE BONDS ON THE KINETICS OF MOLECULAR REACTIONS

Even a cursory analysis of the experimental information on the kinetics of molecular reactions shows that π-bonds are involved in the reaction in the vast majority of cases. It is therefore natural to expect that energy effects due to the peculiarities of behaviour of π-electrons would be revealed in the height of the potential barrier to the reaction. This is in fact so, and here we shall examine the effect of conjugation and cumulative π-bonding on the kinetics of molecular reactions. The influence of conjugation is shown most distinctly by comparing the experimental activation energy with the additive value calculated without correcting for conjugation. For the isomerisation of 3,7-dimethylocta-1,6-diene into 1-isopropenyl-2,3-dimethylcyclopentane, the activated complex of which contains two conjugated π-bonds,



for example, the experimental activation energy is $E_{exp} = 35.2$ kcal[198], whereas the additive value calculated without regard to conjugation is 58 kcal.

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Reactivity of Radicals and Molecules in Radical Reactions

Yu.L.Spirin

A survey is made of the effect of polar interactions, due to substituents and the medium, on the reactivity of radicals and molecules in radical additions (polymerisation of monomers), and the metathesis and decomposition of molecules. Analysis of experimental information by the perturbation method leads to the conclusion that the reactivity of radicals increases, while that of molecules falls, with increase in their electronegative properties produced by the introduction of substituents, interaction with the solvent, etc. The non-additivity of the polar effect of substituents, which is known from the copolymerisation of vinyl monomers, is apparent also in several other reactions. A list of 94 references is included.

I. INTRODUCTION

If only physical constants are used, the description of a reacting system by the equations of quantum physics cannot give solutions which are suitable for practical application to complicated systems. This led to the need to introduce parameters of the hypothetical constants for a given configuration of atoms and electrons, such as the Coulombic and exchange integrals. As the result of the work of London[1] and of Eyring[2] this way of stating the problem for radical reactions enabled the valence bond method to be used to decipher the nature of the activation barrier in chemical reactions and to estimate the rate constant of the exchange between a hydrogen atom and a hydrogen molecule. A significant consequence of this work for an understanding of any radical reaction was the possibility of regarding activation energy as the superposition of bonding and antibonding terms. Analysis of radical reactions from this point of view permitted the extremely important Polanyi–Semenov rule to be formulated[3], which enabled the activation energy of a radical reaction to be estimated from the properties of the reactants. Comparison of this rule with experimental results showed that it had several significant exceptions[3]. Several of them can be described by regarding the rule as a consequence of the London relation and introducing the polarisability as an additional parameter[4]. The need to consider polarisability indicates that the higher unoccupied orbitals of the reactants have a considerable effect on the activation energy. However, no soundly based analysis of the dependence of activation energy on the properties of the reactants has been undertaken by the valence bond method, apparently owing to the difficulties of allowing for the large number of structures necessary for calculating the energy of a complicated polyatomic system of variable configuration.

The molecular orbital (MO) method provides considerably greater opportunities for ascertaining the dependence of reactivity on the structure of the reactants. With atomic orbitals as basis, however, the molecular orbital method does not enable the concept of activation barrier to be formulated, because incorrect allowance is made for the antibonding terms. In the analysis of radical reactions by the molecular orbital method[5-7], therefore, it is postulated that the activation energy E is related to some parameter Z of the system, which can be calculated by the molecular orbital method, using the relation

$$E = C + \alpha Z \qquad (1)$$

where C is constant for a given series of reactions of the same type, and α is a coefficient of proportionality.

The energies of localisation, stabilisation, hyperconjugation, etc. have been used as Z. A feature of the Z parameters is that by means of them the effect of a substituent as a whole is described, without separating it into components, e.g. into polar and resonance interactions. A satisfactory description of experimental results can usually be obtained, this being achieved in several cases by a "happy choice" either of the characteristics of the atoms or of the parameter Z.

The relation (1) can be satisfied if bonding and antibonding terms are connected by a linear dependence, which cannot be correct in general, since during the reaction these terms depend on different variables. Such proportionality is apparently observed in some reactions of a given type. Thus the relation (1) is observed in the polymerisation of vinyl hydrocarbons and in the abstraction of a hydrogen atom from hydrocarbons, whereas departures from this relation are found in the polymerisation of vinyl compounds containing heteroatoms[5,6,8].

Bazilevskii[8] has recently been able to overcome certain difficulties and show that the effect of the antibonding terms can be allowed for in the molecular orbital method. An activation barrier arises, in molecular orbital calculations on a reaction, if we pass by some method from a non-orthogonal set of atomic orbitals to an orthogonal set, i.e. if we make more correct allowance for repulsion between the reactants. In this case an expression is obtained for the energy of a system having non-zero activation energy in Pople's approximation. By using generally accepted assumptions this author[8] has calculated the activation energy for the reaction of the methyl radical with ethylene and has also described the effect of substituents on the activation energies of the polymerisation of several vinyl compounds.

In spite of the attractiveness of semi-empirical methods for calculating the activation energies and the rate constants of chemical reactions, their application to actual systems is at present essentially illustrative in character, since the large number of approximations in the values of atomic and bond parameters, both in the initial and especially in the transition states, leads in several cases to indeterminate results and divergence from experiment. As a consequence the advantages of the method, consisting in the possibility of calculating the effect of differential changes in the structure and the composition of the reactants on the rate of the reactions, have not yet been effectively realised. A considerable amount of work is evidently still necessary on evaluating atomic and bond parameters and elucidating the form of dependence of reactivity on these parameters before it will become possible to investigate reactions by a method of calculation.

An empirical method of investigating reactions, which has been termed the principle of the linear dependence of free energy of activation on structural parameters[9,10], has acquired great practical value. It is based on the hypothesis that the influence of fragments of molecules and radicals (ions) which remain unchanged during the reactions, i.e. substituents at the reaction centre, can be divided into three independent types of interaction—steric, polar (inductive), and resonance—and that the effectiveness of a substituent in the corresponding interaction can be determined by one parameter. Because of the impossibility of an unambiguous separation of the forms of interaction, these parameters have no physically based units of measurement, and are determined as relative values from reactions chosen as a standard. Only polar interactions could in practice be described with satisfactory accuracy, and scales of polar (inductive) constants compared for the substituents. The existing Hammett, Taft, etc. constants[9] differ mainly in the way in which allowance is made for the effect of conjugation. It is possible also to set up scales for the effectiveness of substituents for conjugation (resonance) with the reaction centre. Thus the Q scale is known for describing the ability of vinyl monomers to undergo copolymerisation[11]. Steric interactions cannot be described by a single scale.

Mathematically this principle is equivalent to expanding the free energy of activation $\Delta F^{\neq}$ in a series involving the parameters X_i describing the properties of the structure:

$$\Delta F^{\neq} = \Delta F_0^{\neq} + \frac{\partial \Delta F^{\neq}}{\partial X_i} dX_i + \frac{\partial^2 \Delta F^{\neq}}{\partial X_i^2} dX_i^2 + \ldots \qquad (2)$$

and to the assumption that the first approximation, i.e. retention of terms in the first derivatives, is sufficient to describe the experimental results. Since the free energy of activation depends both on the entropy and on the energy of activation, which in general are not interrelated, and all types of interaction are involved in the reaction, the successful description of a series of reactions using only one variable as its first derivative, must be regarded as the exception rather than the rule. Actually, a so called "compensation effect" is evident in many cases, represented by a linear dependence of the variation in energy and entropy of activation, conjugation and polarity, etc. There are reactions for which taking only the first approximation (additive action of substituents) into account is insufficient. The well studied radical copolymerisation of vinyl monomers is described only by allowing for the non-additive polar interaction of the substituents (the Alfrey–Price relation[5,11]), which corresponds formally to the second approximation (2). In view of the fact that non-additivity of the substituent effects may appear in other reactions, and of the arbitrary character of the separation of the overall effect of substituents into polar and resonance components, it is more correct to regard the influence of substituents as a small perturbation of the reaction centre, which enables non-linear terms in the expansion to be used for the analysis. A new possibility then appears for describing the influence of the structure of the reactants on their reactivity, by calculating the characteristics of the substituents and the constants for series of reactions by semi-empirical methods.

The laws of radical reactions have been more fully studied than those of other reactions, because they vary little with the external conditions. The effect of conjugation on the reactivity of radicals and molecules has been well investigated, and quite satisfactory criteria have been obtained in both the semi-empirical method (stabilisation, localisation, etc. energies) and in the empirical method (heat of reaction)[5-7]. Steric interactions have no common quantitative criteria, which makes their analysis difficult. The σ_S-parameters, introduced by Taft[9], are suitable only for a relatively narrow range of reactions. Information on the effect of steric interactions in homolytic reactions is in most cases qualitative in character and does not allow of generalisation[12]. It may be regarded as fortunate that the steric effect always promotes a decrease in interaction between the reactants, i.e. a decrease in the rate of bimolecular reactions and an increase in unimolecular reactions, so that its role can always be determined qualitatively.

Hardly any general analysis has been made of the effect of polar interactions, in spite of a large number of investigations and also particular relations concerned mainly with the effect of substituents on the activity of molecules. The display of polar interactions in radical reactions and elucidation of the common features thereof constitute the subject of the present Review. Consideration is given to the polar effect of substituents and of the medium on bimolecular substitutions and additions (polymerisation) and the formation of radicals.

II. POLAR EFFECTS OF SUBSTITUENTS IN ADDITION AND SUBSTITUTION

Data on reaction series of radical substitutions and additions are assembled in Table 1. In most of the systems investigated aromatic compounds have been chosen[9] as reactant molecule, the choice of scale (σ) leading to no great differences in the ρ-values for these compounds, as can be judged, for example, from the reaction series 21–25, for which σ and σ^+ scales have been used. This permits a comparative analysis in qualitative form, without the necessity for laborious recalculation. For the additions 13, 14, 46, and 47 the properties of the substituents are characterised by the Taft σ^*-constants. It may be supposed that, since in this case the substituents are separated from the reaction centre by a C=O group, the transfer coefficient of the polar effect through which apparently differs little from the transfer coefficient through a CH_2 group ($\frac{1}{3}$), the range of ρ-values for these reactions is closed to the remaining reactions.

Most reaction series are satisfactorily described by using only one parameter (σ). Only in certain reaction series, e.g. 12, 17, 48, are deviations found, which were explained by conjugation of the substituents with the reaction centre, not taken into account by σ.

It may be noted from Table 1 that the "sensitivity" ρ of the reaction centre is in most reactions negative: i.e. electron-donor substituents in a molecule increase the reaction velocity, whereas electron-acceptor substituents slow down the reaction. The relation of a radical to a molecule in these reactions resembles that of an acid to a base, the role of acid being played by the radical, and that of the base by the molecule. Only for a relatively small number of reactions is $\rho \geqslant 0$: for the addition of benzyl, phenyl, and poly(methyl acrylate) radicals to a double bond (series 12–14, 46–48, 54–56) and for the abstraction of a hydrogen atom by methyl (11) and benzyl (17) radicals. The negative sign of ρ is explained by most authors[5,13,22] by the electron-acceptor properties of the radicals. Indeed, Table 1 shows a tendency for ρ to decrease with increase in the acceptor properties of the radicals. Thus on passing from the benzyl (17, 48) to the methyl (11) and then to the trichloromethyl radical the value of ρ diminishes from +0.8 to −1.75 (26, 45). An analogous tendency is observed with phenylated radicals (52–56). The value of ρ is also

Table 1. Reaction series of radical reactions.

Series No.	Radical	Molecule*	Reaction conditions (t °C, solvent)	Constants: substituent	Constants: reaction series	Ref.
1	$\dot{Br}$	$\overset{\times}{C}H_3$—PhX	80; CCl_4	σ^+	−1.38	13
2	ditto	CH_3—$\overset{\times}{C}H_2$—PhX	ditto	ditto	−0.69	13
3	»	CH_2=CH—$\overset{\times}{C}H_2$—PhX	69.5; chlorobenzene	»	−0.76	13
4	»	(CH_3O_2)—$\overset{\times}{C}H$—PhX	80; CCl_4	»	−0.38	13
5	»	CH_3O—$\overset{\times}{C}H_2$—PhX	ditto	»	−0.35	13
6	»	$PhCH_2O\overset{\times}{C}H_2PhX$	»	»	−0.12	13
7	»	$CH_3O\overset{\times}{C}H$ (PhX) Ph	»	»	0	13
8	$\dot{RO}_2$ **	$(CH_3)_2\overset{\times}{C}HPhX$	90	σ	−0.4	14
9	ditto	$\overset{\times}{C}H_3PhX$	ditto	ditto	−0.6	14
10	$(CH_3)_3C\dot{O}$	ditto	110; γ-picoline	»	−0.5	15
11	$C\dot{H}_3$	»			0	16
12	R (Ph) $C\dot{H}$	$CH_2^{\times}$ = CHPhX	30	σ	0.6	17
13	ditto	$CH_2^{\times}$ = CHCOOX	60	σ*	0.56	18
14	»	$CH_2^{\times}$ = C (CH_3) COOX	ditto:	ditto	0.3	19
15	$\dot{C}Cl_3$	PhCH = CHPhX	105	σ^+	−0.7	20
16	$\dot{S}CH_2COOR$	ditto	ditto	ditto	−0.4	20
17	R (Ph) $C\dot{H}$	$(CH_3)_2\overset{\times}{C}HPhX$	60	σ	0.7	21
18	$R\dot{O}_2$	$\overset{\times}{H}OPhX$	65, styrene	σ^+	−1.49	22
19	ditto	$\overset{\times}{H}O$ (2,6- -t- C_4H_9) PhX	140; 160; oil	σ	−1.01	22
20	»	HOPhX	62.5; chlorobenzene	ditto	−3.7	22
21	»	»	44.4; methyl methacrylate	»	−3.48	22
				σ^+	−2.28	22
22	DPPH***	»	30; benzene	σ^+	−3.22	22
					−2.77	22
23	DPPH***	$\overset{\times}{H}OPhX$	20; CCl_4	σ	−6.4	22
				σ^+	−4.54	22
24	$\dot{R}$	$\overset{\times}{H}SPhX$	110; toluene	σ	−0.433	22
				σ^+	−0.287	22
25	$R\dot{O}_2$	$(CH_3)_2\overset{\times}{C}HPhX$	60; chlorobenzene	σ	−0.54	22
				σ^+	−0.375	22
26	$\dot{C}Cl_3$	$\overset{\times}{C}H_3PhX$	50; chlorobenzene	σ^+	−1.46	22
27	$\dot{Br}$	ditto	80; chlorobenzene	»	−1.39	22
28	ditto	»	29; chlorobenzene	»	−1.78	22
29	$\dot{Cl}$	»	40; benzene, CCl_4	σ	−0.76	22
				σ^+	−0.66	22
30	$(CH_3)_3C\dot{O}$	»	110; γ-picoline	σ	−0.741	22
				σ^+	−0.646	22
31	ditto	»	40; reactants	σ	−0.821	22
				σ^+	−0.695	22
32	$PhCO\dot{O}$	$PhCH_2O\overset{\times}{C}H_2PhX$	80; reactants	σ	−0.957	22
				σ^+	−0.647	22
33	Indophenoxyl****	$\overset{\times}{H}_2NPhX$	30; xylene	σ	−2.53	23
34	»	$\overset{\times}{H}OPhX$			~0	24
35	»	$\overset{\times}{H}O$ — (2,6 -t- -C_4H_9) PhX		σ^+	>0	24
36	$(CH_3)_3C\dot{O}$	$\overset{\times}{H}OPhX$	122; CCl_4	σ^+	−1.19	25
37	»	ditto	122; chlorobenzene	»	−0.74	25
38	»	$\overset{\times}{H}O$ (2,6- -t- -C_4H_9)PhX	122; CCl_4	»	−0.86	25
39	»	ditto	122; chlorobenzene	»	−0.78	25
40	$\dot{Ph}$	$\overset{\times}{C}H_3PhX$		σ^0	−0.5	5
41	$R\dot{O}_2$	ditto		»	−0.77	5
42	Cl	»		»	−0.86	5
43	$\dot{Br}$	»		»	−0.97	5
44	Succinimido*****	»		»	−1.55	5
45	$\dot{C}Cl_3$	»		»	−1.75	5
46	R ($Ph\dot{C}H$)	$CH_2^{\times}$ = C (CH_3) COX		σ*	0.33	26
47	R ($ClCH_2CH_2OCO$)·$\dot{C}CH_3$	ditto		»	0.13	26
48	R (p-CH_3Ph) $C\dot{H}$	$C\dot{H}$ (CH_3) PhX		σ	0.8	27
49	$\dot{O}H$	$\dot{P}hX$		σ	−0.41	28
50	»	$\dot{O}COPhX$		ditto	−0.41	28
51	$\dot{H}$	$\dot{P}hX$		»	−0.7	29
52	p-$NO_2\dot{P}h$	$\dot{P}hX$	20; benzene	»	−0.7	29
53	p-$Cl\dot{P}h$	ditto	ditto	»	−0.27	30
54	$\dot{P}h$	»	»	»	0.05	30
55	p-$CH_3\dot{P}h$	»	»	»	0.08	30
56	p-$CH_3O\dot{P}h$	»	»	»	0.09	30

*The sign × indicates the site of the reaction.

**R is an alkyl radical or a radical linked to the reaction centre by a CH_2 group.

***The diphenylpicrylhydrazyl radical.

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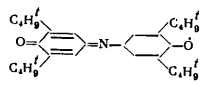

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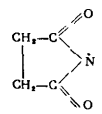


less than zero for electronegative radicals (Br•, Cl•, RO•, RO_2•, R_2N•). The minimum value of ρ is observed with the diphenylpicrylhydrazyl radical, which is apparently explained by the electron-acceptor properties of nitro-groups.

The effect of the structure of the molecule on the value of ρ is less clearly developed. On examining the reaction series 1 and 2, 8 and 9, 13 and 14 we can see that replacing hydrogen by a methyl group in the molecule leads to a decrease in the modulus ρ. For phenols and aromatic amines (18–23, 24, 33–38) the value of ρ is in most cases negative, and for vinyl compounds it is indeterminate (12–16, 46, 47). The magnitude of ρ apparently increases as the electron-donor power of the molecule becomes stronger, but this tendency is very weak.

To analyse the dependence of reactivity on the structure of the reactants, let us expand the reaction rate constant in a series:

$$\lg k_{ij} = \lg k_0 + \left(\frac{\partial \lg k}{\partial \sigma}\right)_R \sigma_i + \left(\frac{\partial \lg k}{\partial \sigma}\right)_M \sigma_j + \left[\left(\frac{\partial}{\partial \sigma}\right)_R \sigma_i + \left(\frac{\partial}{\partial \sigma}\right)_M \sigma_j\right]^2 \lg k + \ldots \quad (3)$$

where k_0 is the reaction rate constant disregarding polar interactions, and σ a measure of the polar properties of the substituents in the radical R and the molecule M, e.g. the Hammett, Taft, Alfrey–Price, etc. constants. Since the Alfrey–Price relation, including terms in $\sigma_i\sigma_j$, is observed in radical copolymerisations, whereas a linear dependence on σ is found with most reactions, it is apparent that in general it is sufficient to confine ourselves to the approximation

$$\lg k_{ij} = \lg k_0 + \rho_R\sigma_i + \rho_M\sigma_j + \rho_{RM}\sigma_i\sigma_j \quad (4)$$

for the rate constant, in which terms in σ_i^2 and σ_j^2 are neglected in comparison with Eqn. (3), in view of their smallness or indistinguishability from terms in σ, while the constants ρ denote the corresponding derivatives with respect to σ.

Experimentally reaction series are usually investigated, in which the relative rate of addition of a molecule containing different substituents to some radical is determined: i.e. the σ_i are constant for a series, and presumably also k_0, this converts formula (4) into

$$\lg \frac{k_{ij}}{k_0} = (\rho_M + \rho_{RM}\sigma_i)\sigma_j \equiv \rho_{exp}\sigma_j \qquad (5)$$

which is formally analogous to the Hammett, Taft, etc. relations. Equation (5) shows that the experimental quantity ρ_{exp} gives no information on the "sensitivity" of the radical to the polar effect of its substituents, since the term in ρ_R is constant in a given series of reactions, and is included in $k_0' = k_0 + \rho_R\sigma_i$. The sign and magnitude of ρ_{exp} give information only on the energy of polar interaction of substituents in the molecule with the radical or its substituents and on the "sensitivity" of the molecule. As already remarked, the magnitude of ρ_{exp} diminishes with increase in the electronegativity of the radical, which can be related to the quantity σ_i. Hence $\rho_{RM} < 0$. If we examine reaction series for different hydrocarbon radicals towards a single series of molecules for which ρ_M is constant, the whole difference in ρ_{exp} is determined by the electronegativity of the substituents in the radical, not by the properties of the radical as such. This is an important confirmation of the correctness of the Alfrey–Price relation in reactions involving detachment of a hydrogen atom. The negative sign of ρ_{RM} is explained by the effect of polar structures on the energy of the transition state in radical reactions, from which it follows that differently charged substituents in radical and monomer lower the energy of the transition state[5].

Existing data do not enable the sign of ρ_M to be assessed. Since for most reactions $\rho_{exp} < 0$ and $\rho_{RM} < 0$, it can be assumed that ρ_M is small and apparently slightly exceeds zero.

To determine ρ_R data are required on the absolute or relative rate constants in the reactions of different radicals with some one molecule. The experimental difficulties in the way of carrying out such a programme are great, which explains the extraordinary sparsity of such data. Bagdasar'yan's monograph[5] gives data on the absolute constants for addition of the radicals $CH_3^\bullet$, $CCl_3^\bullet$, and $CF_3^\bullet$ to hept-1-ene at 60°C, which are respectively 0.0005, 0.00062, and 1.7 $M^{-1}\,s^{-1}$, and which indicate an increase in reactivity of the radicals with increase in the electronegativity of the substituents, this occurring in spite of an increase in the energy of conjugation in the radical on the introduction of substituents. Some conformation of the increase in activity of the radicals with increase in electronegativity is the decrease in activation energy in the detachment of hydrogen from alkanes on passing from the radical $CH_3^\bullet$ to $CF_3^\bullet$.[4] The literature contains hardly any systematic data on the absolute rate constants for reactions involving the detachment of hydrogen. In this connection great significance is acquired by results obtained for the polymerisation and copolymerisation of vinyl monomers, from which reliable values of the relative reactivity of monomers have now been obtained. There are considerably fewer data on the relative reactivity of radicals and on the absolute rate constants, and they are less reliable. Existing data on the absolute rate constants of chain growth can, on certain assumptions concerning the energy of conjugation in the monomers, be described by means of Eqn. (4). With $\rho_{RM} = -1$† it was found[31,32] that $\rho_R = 1.6$ and $\rho_M = -0.35$: i.e. in polymerisation reactions the radical is more "sensitive" than the monomer to the polar effect of substituents, and further the effects of substituents in the radical and in the monomer are opposite in sign. From the fact that $\rho_R > 0$ it follows that electron-acceptor substituents increase the reactivity of radicals, whereas electron-donor substituents diminish it. Indirect data indicate that such a relation cannot be a particular case, but it is characteristic of all radical reactions involving molecules containing substituents at the site of formation of the radical. This generalisation is not valid for the addition of radicals to $\alpha\beta$-substituted vinyl compounds, owing to the change in nature of the interaction of the substituents: i.e. formula (4) is not applicable to such reactions. Thus in the copolymerisation of β-fluorinated styrenes (2), in which the fluorine has relatively little influence on the steric interactions, with styrene itself (1) it is found[35] that $r_1 = K_{11}/K_{12} > 1$, while $r_2 = K_{22}/K_{21} \to 0$, i.e. $K_{22} \to 0$. Formal treatment of these results on the basis of the Q–e (or Q'–e) scheme[31,32] for β-fluorostyrenes yields $e_2 > e_1$ and $Q_2 \to 0$. The latter is, of course, incorrect, since the energy of conjugation in β-fluorostyrenes is close to that in styrene itself, and $Q_2 \simeq 1$. A correct description of such systems needs to take into account terms in the expansion of the expression for the rate constants describing the effect of β-substituents.

Summarising, we can conclude that the introduction of electron-acceptor substituents into a radical, or increasing the electronegativity of the radical, increases its "sensitivity" to polar changes in the molecule, and increases the reactivity of the radical. Electron-acceptor substituents in the molecule (at the site of formation of the radical) change reactivity mainly by polar interaction with the radical or with substituents therein.

III. EFFECT OF THE POLAR PROPERTIES OF SUBSTITUENTS ON THE DECOMPOSITION OF PEROXIDES AND AZO-COMPOUNDS

The influence of the polarity of substituents on the rate constants for decomposition of organic compounds involving the formation of two radicals has been investigated mainly with peroxides and azo-compounds as examples.

The decomposition of substituted benzoyl peroxides was described by Swain and his coworkers[36], who discovered the additive effect of substituents, present in the rings of different aromatic peroxides, on the reaction rate constant:

$$\lg \frac{k}{k_0} = -0.38(\sigma_1 + \sigma_2).$$

These workers also concluded that the term in $\sigma_1\sigma_2$, describing the interaction of the substituents, was small or even absent.

Later investigations[37] have led to the conclusion that the effect of substituents on the decomposition of substituted benzoyl peroxides is described by a more complicated relation, and that conjugation of the reaction centre with a substituent exerts a considerable influence on the decomposition rate constant. Table 2 lists data obtained by different workers[36–38] on the decomposition of peroxides. It shows that electron-donor substituents accelerate decomposition, whereas electron-acceptor substituents slow de-

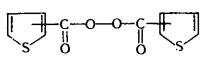
† The calibration $\rho_{RM} = -1$ corresponds to the Alfrey–Price scale for the polar constants of substituents, which are proportional to the Hammett constants[33,34].

composition down. An analogous effect can be observed in the decomposition of saturated per-esters: when chlorine in the α-position to a carbonyl group is replaced by an isopropyl group, the decomposition rate constant increases fourfold[39]. It can also be concluded from these observations that increase in the acceptor properties of radicals should increase their activity in recombination reactions.

Table 2. Decomposition of substituted benzoyl peroxides.

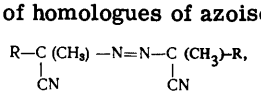
Substituent	10^4k, s^{-1} (at 90°C), from Ref.		
	37	36	38
p-CH_3O	3.29	3.92	5.20
p-CH_3	1.93	2.05	1.98
H	1.33	1.41	1.44
p-Cl	0.94	1.21	1.28
m-Br	1.00	0.81	—
3,4-Dichloro-	1.11	—	—
p-CN	0.97	0.68	0.81
p-NO_2	0.87	—	1.45

An accelerating action of electron-donor substituents has been observed[40] in the decomposition of substituted dithenoyl peroxides of general formula

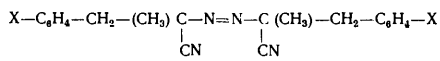


The observed relations are consistent with the tendency of the energy of the O–O bond, which is equal to the activation energy for decomposition of the peroxide, to decrease on passing from hydrogen peroxide to alkyl peroxides[41].

Several investigations[42–44] have been made on the effect of substituents on the decomposition of azo-compounds. Overberger et al.[43] found that the effect of substituents on the decomposition of homologues of azoisobutyronitrile

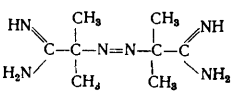


where R = CH_3, C_2H_5, n-C_3H_7, iso-C_4H_9, can be explained by steric causes. In another investigation Overberger and his coworkers[42] found that the substituent in compounds of the type



where X = Cl, H, NO_2, has a weak polar effect.

The substituent has been found to have a considerable effect in the thermal decomposition (at 60–85 °C of azoisobutyramidine



and its nitrates[44]. The addition of one molecule of nitric acid produces a very considerable increase in the rate of decomposition of this compound. Addition of a second molecule of the acid also leads to an increase in the rate of decomposition, but the effect is less marked. Decomposition of the azo-compound and its salts apparently takes place entirely by a radical mechanism, since, when the reaction is conducted in the presence of methyl methacrylate, the latter polymerises at a rate which parallels the rate of decomposition. Since the addition of acid to an amidino-group is equivalent to increasing the electron-acceptor properties of the substituent, the effect of the polarity of the substituent on the decomposition of this compound is formally opposite to the effect of substituents on the decomposition of peroxides, which appears improbable. A possible explanation of the accelerated decomposition of azoisobutyramidine on interaction with an acid is an increase in energy of conjugation in the substituent, which tends to stabilise the radicals and hence diminish the energy of the C–N bond.

IV. EFFECT OF THE MEDIUM ON RADICAL ADDITIONS AND SUBSTITUTIONS

The interaction of radicals with the medium, by which will be understood any set of molecules which do not react directly, including one complexing molecule, can take place in two ways—(1) by interaction of the atom carrying the unsatisfied valency with the medium, and (2) by interaction of substituents on the radical with the medium. A recent review[45] has discussed several radical reactions in which the effect of the medium is evident. In the present Review the effect of the medium is examined as a function of the structure of the radicals and the molecules.

There are few investigations in which the direct effect of the medium on an atom carrying the unpaired electron has been observed experimentally. Most of the systems described relate to reactions in which the radical is a free or substituted heteroatom, e.g. Cl or RO, having a lone pair of electrons directly on the atom containing the unpaired electron. Interaction of such radicals with the medium takes place mainly either by a mechanism of hydrogen bonding or by complex formation with the π-bonds of the solvent. The complicated electronic structure of radicals does not allow the nature of the interaction to be determined unambiguously[45]. Russell[46], who observed that the aromatic character of the solvent influenced the reactivity of the chlorine atom, suggested that a linear relation should exist between the ionisation potential of the radical and the energy of its interaction with the solvent. Investigations of the reactivity of the chlorine atom and of the t-butoxy-radical showed that in aromatic solvents the activity of the radicals diminished with increase in the basic character of the medium. It is significant that the effect of the solvent is considerably more strongly developed on the chlorine atom than on the alkoxy-radical[46,47]. Other investigations[48,49] on the effect of solvents on the activity of the t-butoxy-radical showed a considerably stronger solvent effect. However, while investigating the reaction of the t-butoxy-radical with substituted toluenes in different solvents, Sakurai and Hosomi concluded[49] that the solvent, although strongly influencing the ratio of the rate constant for reaction of the radical with toluenes to the rate constant for decomposition of the t-butoxy-radical into acetone and a methyl radical‡, has little effect on the value of ρ in a series of reactions. Thus values of −0.35, −0.32, and −0.39 were obtained for ρ for Freon-113, chlorobenzene, and acetone at 45°C, whereas the above ratio of the constants for this series of solvents is respectively 2.19, 1.31, and 0.52. From these observations it was concluded[49] that the solvent has a greater effect on the decomposition of the t-butoxy-radical than on its ability to abstract a hydrogen atom. In the opinion of these workers, the effect of the solvent on the reactivity of the radical is described by the variation in ρ with the solvent, and is therefore

‡ The reactivity of the t-butoxy-radicals was determined[47,48] by the method of competing reactions, on the assumption that the decomposition constant of the t-butoxy-radical is independent of the solvent.

small. Investigation of the effect of solvents on the decomposition of oxygen-containing radicals[45] showed that the rate of decomposition of such radicals depended on the presence of hydrogen bonds between the radical and the solvent.

In comparison with heptane, pyridine has been found[50] to have an activating effect, and ethylbenzene a deactivating action, on the reactivity of certain nitric-oxide radicals, in particular on that of the bismethoxyphenylnitrogen oxide radical toward 2,6-di-t-butylphenol. It is assumed[50] that the solvents form π-complexes with the radical. According to spectrophotometric data the heat of complex formation with benzene is 6.2 and 7.5 kcal mole^{-1} in ground and excited states[51].

To ascertain the nature of the effect of the medium it is extremely interesting to examine the action of solvents on the polymerisation and copolymerisation of vinyl monomers, since in this case the atom carrying the radical contains no lone pairs of electrons, which simplifies the pattern of interaction of the radical with the medium. As early as the end of the 1940s the influence of the medium on radical copolymerisation constants was investigated[11] in connection with the parameter e in the $Q-e$ scheme. It was established that copolymerisation constants, measuring the relative activity of the monomers, were independent of the solvent. In particular, such independence was found for the styrene–methyl methacrylate system, copolymerisation of which was conducted in benzene, acetone, and methanol[52]. It follows from these data that the reactivity of hydrocarbon radicals is independent of the properties of the medium. This postulate has become widely accepted, and on its basis vinyl monomers have been classified according to the $Q-e$ parameters[5,11], which represent the reactivity of the monomers. It should be noted that experimental errors in determining the composition of copolymers are fairly substantial, and it is highly probable that the solvent effect will be hidden by these errors. Several investigations have recently been made on the effect of the nature of the solvent on the kinetics of the polymerisation of styrene and methyl methacrylate. In a study of the polymerisation of methyl methacrylate in aromatic solvents, initiated by azoisobutyronitrile, the rate of breakdown of which is practically independent of the solvent[53], Burnett and his coworkers[54] found that the rate of polymerisation increases in the series of solvents—benzene, chlorobenzene, bromobenzene, iodobenzene—by more than 50%. They consider that the solvent, while not affecting the decomposition of the initiator, nevertheless influences the efficiency of initiation by the fact that radicals formed by decomposition of the initiator react with the solvent. In a later paper Burnett et al.[55] have examined the effect of tri- and tetra-halogenated benzenes. It was found that disubstituted benzenes have a greater effect on the rate of polymerisation than have monosubstituted compounds, whereas tri- and tetrasubstituted benzenes have hardly any effect on the rate of polymerisation. In no case was incorporation of the solvent into the polymer observed, which might have indicated an effect of the medium on the reaction by a mechanism of chain transfer. It is curious that the above solvents do not affect the rate of polymerisation when the reaction is initiated by benzoyl peroxide[54]. This supports the view that the solvent influences the efficiency of initiation.

A criticism has recently appeared[56] of the views of Burnett et al. on the mechanism by which the medium affects the polymerisation of methyl methacrylate. The experimental results are confirmed, but it is concluded that the influence of the medium on this process, as on the polymerisation of styrene investigated previously[57], can be explained by the hypothetical formation of a charge-transfer complex between the growing radical and the monomer or the solvent. According to these authors[57] the rate of chain growth V_{gr} is proportional to the concentration of the radical–monomer complex:

$$V_{gr} = K_{gr}[R][M] = K'_{gr}[RM]$$
$$[R] = [RM] + [RS]$$

where R is the free radical, M the monomer, S the solvent, and RM and RS are the complexes formed by the radical with the monomer and with the solvent respectively.

Introducing the mean lifetimes of the complexes τ_M and τ_S and taking into account the stationary state conditions $[RM]/[RS] = \tau_M[M]/\tau_S[S]$, the authors derive an expression for the rate of chain growth:

$$V_{gr} = K_{gr}[R][M] \cdot \varphi^{+}_{gr}, \text{ where } \varphi^{+}_{gr} = \frac{[M]_{S=0}}{[S] \cdot \tau_S/\tau_M + [M]},$$

while $[M]_S = 0$ is the initial concentration of the monomer during bulk polymerisation.

The quantity φ^{+}_{gr} can provide information on the interaction of the radical with the medium. It is determined experimentally from the expression for the rate of polymerisation $V_{pol} = (V_{in}/K_0)^{\frac{1}{2}}[M]\varphi^{+}_{gr}$ or from the corresponding expression for the degree of polymerisation. Using the value obtained for φ^{+}_{gr}, we determine τ_S/τ_M from the relation

$$\frac{[M]_{S=0}}{\varphi^{+}_{gr} \cdot [M]} = 1 + \frac{\tau_S [S]}{\tau_M [M]} .$$

Table 3 gives these authors' results for several solvents.

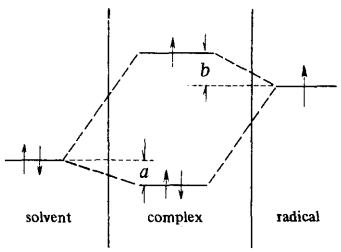
Table 3. Effect of solvents on the polymerisation of styrene (1.82 M at 50°C with azoisobutyronitrile as initiator)[57].

Solvent	φ^{+}_{gr}	τ_S/τ_M	Solvent	φ^{+}_{gr}	τ_S/τ_M
Bromobenzene	1.01	0.93	Dimethylformamide	0.77	0.91
Anisole	0.97	0.97	Toluene	0.77	1.28
Dioxan	0.91	0.87	Methylene chloride	0.72	0.83
Pyridine	0.86	0.87	Tetrahydrofuran	0.7	1.09
Tetrahydropyran	0.9	1.01	Methyl isobutyrate	0.7	1.53
Ethylbenzene	0.84	1.28	Butanone	0.69	1.22
1,2-Dichloroethane	0.84	0.85	Dimethoxyethane	0.66	1.52
Chloroform	0.8	0.90	Ethyl acetate	0.65	1.44
Benzene	0.8	1.04	Styrene	—	1.00
Mesitylene	0.79	1.62			

The idea[57] that the solvent effect is due to complex formation with the radical is supported also by the work of Bamford and Brumby[58], who have investigated the polymerisation of methyl methacrylate in aromatic solvents at 25°C. They find that complex formation influences both the rate constants for chain growth and for chain termination, although the effect is small. Thus the growth rate constant increases from 260 to 330 M^{-1} s^{-1} on passing from benzene to benzonitrile. The diminution in the reaction velocity by solvents parallels their capacity for π-complex formation, and varies in the sequence—benzene > fluorobenzene > chlorobenzene > bromobenzene > benzonitrile.

The tendency of radicals to undergo reactions mainly with aromatic solvents indicates $\pi\pi$-interaction rather than

polar (acceptor or donor) interaction. According to Russell[46] the activity of the chlorine radical falls with decrease in the electronegativity of the substituents in the aromatic solvents. A similar tendency can be observed also in polymerisations. This indicates that the radical acts as an acceptor of electrons in the π-complex. It may be supposed that a π-complex is formed mainly by the superposition of a non-bonding orbital of the radical, in which is located the unpaired electron, with a higher occupied orbital of the solvent, which, as is evident from the diagram, leads to a gain in energy ($E = 2a + b > 0$), and hence a diminution in the activity of the radical. The energy of interaction in the complex is 6 kcal mole^{-1}.[59] However, experimental data indicate the almost complete absence of delocalisation over the solvent of the unpaired electron in complexes of stable radicals with solvents[45], which is inconsistent with participation of the non-bonding orbital of the radical in formation of the complex.



Formation of complex between radical and solvent.

A very curious effect of organoboron compounds on the polymerisation of vinyl monomers has been reported[60,61]: Arimoto[60] discovered that, in the presence of aliphatic organoboron compounds, polymerisation of the monomers—styrene, methyl methacrylate, acrylonitrile, and vinyl acetate—is not inhibited by typical inhibitors of radical processes, e.g. quinol, *N*-phenyl-2-naphthylamine, etc., even when present in excess relative to the organoboron compound. He suggests that the radical forms a complex with the organoboron compound. This complex is reactive towards the monomer and inactive towards inhibitors. Triarylborons do not produce such effects.

The effect of hydrogen bonds on the reactivity of radicals localised on heteroatoms has been examined in a review[45], where it is stated that "... in all cases, when a 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 decreased activity of the radicals must evidently be attributed to steric causes, since, owing to the predominance of electrostatic forces in a hydrogen bond, the energy of the ground state of the radical is lowered, and consequently its reactivity is increased. A solvating molecule impedes the access of reactant molecules to the radical, thereby diminishing the reaction velocity.

Hydrogen bonds have been found to influence the kinetics of radical reactions in the polymerisation of several vinyl monomers containing heteroatoms. On complex formation between the monomer and a hydroxylated solvent through a heteroatom, the change in electronegativity of the heteroatom in the monomer produces a change in the charge distribution, which leads to a change in the polar properties of the double bond and in some cases a change in the conjugation energy. When the monomer becomes a radical as a result of the reaction, the energy of the hydrogen bond is somewhat modified, which complicates interpretation of available results. However, this effect is apparently small, and the characteristics of atoms involved in the hydrogen bond can be assumed to remain unchanged during the reaction. This permits the application to these systems of various correlation formulae.

As remarked above, the composition of copolymers of styrene with methyl methacrylate is unaffected by changing the medium from benzene and acetonitrile to methanol, which indicates that hydrogen bonds have no effect on the reactivity of methyl methacrylate[52]. The rate of polymerisation of *N*-vinylpyrrolidone is increased by conducting the process in aqueous solution, which produces an increase in molecular weight[62], this indicating either a change in the rate constant of chain growth or a decrease in the rate constant of chain termination. Direct experimental evidence of a change in the reactivity of monomers and the corresponding radicals on formation of hydrogen bonds with the solvent was obtained by Ryabov and his coworkers[63]. They found that the composition of styrene–2-vinylpyridine, styrene–methacrylic acid, and methyl methacrylate–methacrylic acid copolymers depends on the nature of the solvent. Subsequent investigations by other workers[64,65] have confirmed these observations. The published data are listed in Table 4. They show that the monomers—vinylpyridines and vinylpyrrolidone—which are electron donors with respect to hydroxylated solvents, are characterised by an increase in the acceptor properties of the substituent (increase in e) with increase in the acidity of the solvent. Acrylic and methacrylic acids, on the other hand, exhibit a diminution in electron-acceptor properties with increase in the basic strength of the solvent. Variation in the properties of the solvent probably affects also the value of Q, which in most cases increases with increase in e. However, this tendency is not clearly defined, and for several systems (Table 4) Q remains unchanged with variation in e. The change in Q produced by varying the solvent indicates that variation in the polarity of the substituent leads to a change in the energy of conjugation in the monomer: i.e. Q and e are not independent quantities, as is assumed in the Q–e scheme. However, these observations require confirmation.

In several cases the rate of polymerisation of monomers has been found to vary with the properties of the medium. Thus the rate of homopolymerisation of methacrylic acid diminishes on the addition of dimethylformamide[63]. Increase in the pH of the medium has been found[68] to decrease the rate constant of chain growth K_{gr} in the polymerisation of acrylamide. The rate of polymerisation of this monomer depends also on the nature of the solvent[59]: the value of $K_{gr}/K_0^{\frac{1}{2}}$ decreases in the sequence—water, dimethyl sulphoxide, tetrahydrofuran. The reason for the change in the rate of polymerisation of *N*-vinylpyrrolidone when dichloroethane is replaced by methanol is the change in K_{gr} due to the diminished electron-donor properties of the pyrrolidone ring. The observed doubling of K_{gr} shows good qualitative correlation with Eqn. (4).

Several interesting results have recently been obtained on the effect of metal salts on the activity of monomers in radical polymerisation. As early as 1957 Bamford et al.[69] reported that a lithium salt accelerates the polymerisation

of acrylonitrile. Several papers have since been published on the influence of salts of zinc [70-75], cadmium [74], mercury [73], and aluminium [76-78].

Table 4. Effect of hydrogen bonds on reactivity of monomers in copolymerisations.

Monomers M_1	Monomers M_2	Solvent	r_1	r_2	Q_2	e_2	Ref
Styrene $Q=1$ $e=-0,8$	2-vinylpyridine	—	0.57	1.33	(1.16)	(−0.285)*	63
		ethanol	0.486	0.862	(0.55)	(0.13)	63
		methanol					
		phenol	0.426	0.607	(0.93)	(0.36)	63
		acetic acid	0.253	0.549	(1.29)	(0.6)	63
			0.16	0.36	(1.62)	(0.89)	6
Styrene	4-vinylpyridine	—	0.78	1.1	1.12	−0.72	66
		acetic acid	0.1	0.34	3.1	1.35	66
Methyl methacrylate	ditto	—	0.42	0.65			66
		acetic acid	0.24	0.55			66
ditto	2-vinylpyridine	—	0.48	0.68	1.35	−0.7	66
		acetic acid	0.43	0.3	1.80	1.3	66
Styrene	methacrylo-2,5-methylvinylpyridine	—	0.88	1.1	1.1	−0.8	66
		acetic acid	0.73	0.76	1.0	−0.2	66
Methyl methacrylate	ditto	—	0.42	0.58			66
		acetic acid	0.47	0.75			66
Styrene	methacrylic acid	—	0.2	0.66	(1.60)	(0.62)	63
		dimethylformamide	0.53	0.45	(0.73)	(0.4)	63
Methyl methacrylate $Q=0.74$ $e=0.4$	ditto	—	0.55	1.55	(1.58)	(0.8)	63
Methyl methacrylate $Q=0.74$ $e=0.4$	methyl methacrylate	dimethylformamide	0.98	0.68	(0.59)*	(−0.24)	63
Styrene	acrylic acid	—	0.25	0.07	0.94	1.01	64, 65
		butan-2-one	0.7	0.15			
		dioxan	0.75	0.13	0.39	0.73	64, 65
		tetrahydrofuran	0.9	0.14	0.35	0.64	64, 65
		dimethylformamide	1.03	0.15	0.33	0.57	64, 65
Methyl methacrylate	ditto	—	1.86	0.24	0.31	0.81	64, 65
		benzene	1.5	0.2			
		dioxan	2.32	0.3	0.25	0.65	64, 65
		tetrahydrofuran	2.46	0.25	0.24	0.61	64, 65
		dimethylformamide	2.89	0.24	0.2	0.51	64, 65
Vinyl chloride	*N*-vinylpyrrolidone	dichloroethane	0.55	0.34	0.066	−1.1	67
		methanol	0.74	0.73	0.052	−0.6	67

*Values in parentheses have been calculated by me from the values given for r_1 and r_2.

Imoto and his coworkers [70,71] have found that during polymerisation methyl methacrylate forms an active complex MMA.$ZnCl_2$ in the presence of zinc chloride. Copolymerisation constants have been determined for this complex with vinylidene chloride, whose activity is unaffected by zinc chloride, and the parameters Q and e have been calculated (Table 5). These workers have investigated also the effect of zinc chloride on the polymerisation of acrylonitrile.

Okamura and his coworkers [73-75] have made a series of studies of the effect of complex formation with metal salts on the reactivity of vinylpyridines. They find that complexes are formed containing two molecules of the monomer and one molecule of the salt. The rate of polymerisation of the complex is higher than that of the pure monomer. The increase in rate is assumed to be due to an increase in K_{gr}. For 4-vinylpyridine the accelerating effect increases in the sequence [74]

$$Cd(CH_3COO)_2 > ZnCl_2 > Zn(CH_3COO)_2 > ZnBr_2 > ZnI_2$$

which is almost the same as the sequence for 2-methyl-5-vinylpyridine [73]. Values of Q and e for vinylpyridines included in Table 5, have been determined for copolymerisation with styrene, which does not form complexes with metal salts.

Table 5. Effect on the reactivity of monomers of complex formation with metal salts.

M_1	M_2	T, °C	r_1	r_2	Q_1	e	Ref.
MMA*	CH_2CCl_2	60	2.5	0.5	0.74	0.4	71
MMA + 0.089 $ZnCl_2$	ditto	60	12	0.08	2.82	0.8	71
MMA + 0.214 $ZnCl_2$	»	60	20	0.04	6.63	1.1	71
4-VP**	styrene	50	0.52	0.54	0.82	−0.2	74
4-VP + $Zn(CH_3COO)_2$	ditto	50	2.7	0.08	4.7	0.44	74
2-VP	»	50	0.9÷1.81	0.55	1.3	−0.5	74
2-VP + $Zn(CH_3COO)_2$	»	50	3.55	0.55	$r_1 \cdot r_2 =$	1.84>1	74
2-Methyl-5-VP	»	50	0.68	0.6÷0.88	0.99	−0.58	74
2-Methyl-5-VP + + $Zn(CH_3COO)_2$	»	50	2.0	0.35	1.75	−0.26	74

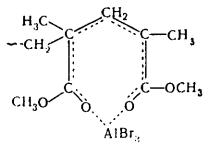
*MMA = methyl methacrylate.
**VP = vinylpyridine.

Direct confirmation of the increase in K_{gr} on complex formation between methyl methacrylate and zinc chloride has been obtained by Bamford et al. [79], who find that at 25°C the value of K_{gr} increases from 250 M^{-1} s^{-1} for the pure monomer to 610 M^{-1} s^{-1} for its complex.

A characteristic feature of the monomer–metal salt complexes investigated is the simultaneous increase in the parameters Q and e relative to the pure monomer (Table 5). This indicates the complicated nature of the interaction between metal salts and monomers, caused by the formation of a single system of molecular orbitals in the complex compound. Examination of the electronic absorption spectra showed that the complexes exhibit a red shift in the $\pi-\pi$ transition as compared with the pure monomer [75]. The magnitude of the displacement correlates with the value of Q. An attempt has been made to examine the structure of the complexes by the method of molecular orbitals [94].

The effect of Lewis acids on the reactivity of monomers has been investigated in the copolymerisation of acrylonitrile and methyl methacrylate [76,77]. Addition of aluminium chloride led to a decrease in the acrylonitrile content of the copolymer. The complex of acrylonitrile with aluminium chloride proved to be incapable of homopolymerisation, which must apparently be attributed to electrostatic repulsion between the radical and the monomer. The photoinitiated polymerisation of methyl methacrylate in the presence of aluminium chloride and aluminium bromide revealed [78] a considerable increase in the rate of the process compared with polymerisation of the pure monomer, which was ascribed to increase in K_{gr} due to the coordinating action of the aluminium salt. Use of electron spin resonance in the same investigation established that the unpaired electron is

partly transferred to the aluminium atom. The following scheme is suggested [78] for the transition state in chain growth



according to which growth is accelerated by coordination of the monomer and the radical.

The interaction of acrylonitrile with ethylaluminium dichloride [80] leads to the formation of a 1 : 1 complex. It is remarkable that the complex is incapable of homopolymerisation, but copolymerises well, e.g. with propene to form an alternating 1 : 1 copolymer. The alternation may be caused by the formation of a charge-transfer complex between the monomers. The possibility of the formation of such complexes must in general be taken into account in ascertaining their reactivity, since considerable anomalies may be observed. For example, it has proved possible to copolymerise 1,4-dioxen with maleic anhydride [81], although neither monomer polymerises separately by a radical mechanism; their copolymerisation was made possible by complex formation.

Thus the polar effect of the medium on the reactivity of radicals and molecules, effected through hydrogen bonds, complex formation with metal salts, etc., can be identified with the change in the properties of the substituents, and described by Eqn. (4). The nature of the change in the energy of radicals on π-complex formation with solvents and on interaction with electron pair acceptors, such as organoboron compounds, is obscure. It may be supposed that π-complex formation is accompanied by a decrease in the energy of the radical caused the solvent utilising a non-bonding orbital of the radical.

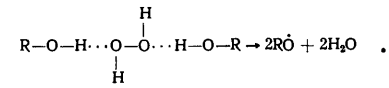
V. EFFECT OF SOLVENTS ON THE THERMAL DECOMPOSITION OF AZO-COMPOUNDS AND PEROXIDES

The influence of solvents on the unimolecular decomposition of molecules has been investigated on the decomposition of peroxides and azo-compounds, which are initiators of various radical processes.

Arnett [82] investigated the thermal decomposition of azoisobutyronitrile in various solvents, and found the rate constant to vary little with the solvent. In a thorough investigation Morou [53] also detected only a slight variation in the rate constant for the decomposition of azoisobutyronitrile with the nature of the solvent. Thus in the series of solvents—methyl methacrylate, xylene, cyclohexanol, dioxan, *o*-dichlorobenzene, and dimethylformamide—the decomposition rate constants at 60°C were respectively (8.40, 10.40, 12.5, 8.70, 11.0, and 10.94) $\times 10^{-6}$. Because of the unsystematic collection of solvents, these results are insufficient to determine the effect of solvents. An attempt to interpret the effect of solvents on the decomposition of phenylazotriphenylmethane was unsuccessful [83].

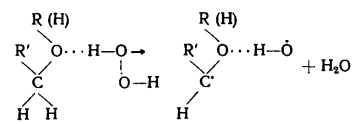
The effect of solvents on the decomposition of benzoyl peroxide is discussed in Bagdasar'yan's monograph [5]. Analysis of the experimental data shows that this compound tends to undergo chain decomposition. At low concentrations of the peroxide or in the presence of inhibitors the decomposition rate constant is almost independent of the solvent. An appreciable solvent effect is observed in the decomposition of t-butyl 2,3-dipropylcycloprop-2-eneper-carboxylate [84]. The rate of decomposition increases in the sequence—ethylbenzene, chlorobenzene, benzonitrile, acetonitrile, benzyl alcohol.

Complicated phenomena are observed in the decomposition of hydroperoxides, including hydrogen peroxide, in various solvents. The energy of the O–O bond is 48 kcal mole^{-1} in hydrogen peroxide [85], and rather lower (42 kcal mole^{-1}) in aliphatic hydroperoxides [41]. In an investigation of the thermal decomposition of butyl and cumene hydroperoxides Stannett and Mesrobian [86] observed an accelerating effect with alcohols, ethers, acids, and vinyl monomers in comparison with benzene, cyclohexane, carbon tetrachloride, chloroform, chlorobenzene, and even pyridine. The authors did not suggest any mechanism to explain the effect of the solvents. Later investigation of the decomposition of hydroperoxides [87–93] have yielded additional data enabling the reaction mechanism to be assessed to a certain extent. It was ascertained that in active solvents the activation energy of the decomposition of hydroperoxides is lowered to around 20 kcal mole^{-1}, [88–92] which is 15–20 kcal mole^{-1} lower than the value in the gas phase and apparently in inert solvents [41,85]. To explain such a large energy discrepancy it has been suggested [88,89] that in alcohol it is not a hydroperoxide molecule but its complex with the solvent which decomposes:



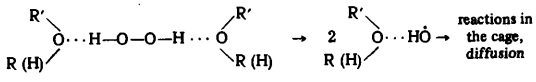
According to this scheme simultaneous cleavage of three bonds and the formation of two new bonds take place in the activated complex. The scheme provides an explanation of the decrease in activation energy of decomposition, but is inconsistent with the formation of terminal hydroxy-groups in the oligodienes obtained by initiating the polymerisation of dienes with hydrogen peroxide in methanol [91].

It was also found [91] that replacing the alcohol by tetrahydrofuran has little effect on the rate or the efficiency of initiation, but substantially affects the concentration of hydroxyls in the polymer. In the opinion of the authors the following scheme for the transition state



which takes into account solvation of the peroxide by the solvent, enables the observed phenomena to be understood. According to this scheme the low efficiency of initiation is explained by the abstraction of α-hydrogen atoms from the solvent and subsequent recombination of the resulting radicals in the cage. The diminished concentration of hydroxyls in the polymer is also explained by instantaneous transfer of the radical to the solvent on formation. Since the transfer reaction is exothermic, and can occur at the same time as cleavage of an O–O bond, the decrease in activation energy for decomposition of the peroxide can also be explained. According to later, unpublished results obtained by the same workers [91], however, polymerisation of dienes initiated by hydrogen peroxide is observed also in solution in t-butyl alcohol which has no α-hydrogen atom, and occurs at the same rate as in methyl alcohol, leading to the formation of oligomers containing two terminal hydroxy-groups. This indicates that abstraction of an α-hydrogen atom is independent of cleavage of the O–O bond.

With all the above facts taken into account, the suggestion is made that hydrogen peroxide (and hydroperoxides) decompose according to the scheme



the realisation of which requires that the energy of interaction of the hydroxyl radical with the heteroatom of the solvent should be increased by 10–15 kcal mole^{-1} as compared with the energy of a hydrogen bond. This increase in interaction energy is possible as a consequence of the formation of complexes analogous to charge-transfer complexes or π-complexes (see diagram).

Acceleration of the decomposition of hydroperoxides is observed also in hydrocarbon solvents containing double bonds[89-93]. The acceleration apparently results mainly as a consequence of the reaction

$$ROOH + H_2C{=}CHR_1 \rightarrow HOCH_2{-}\dot{C}HR_1 + \dot{O}R$$

suggested by Denisov[92], in which the vinyl compound acts as an electron donor. Walling and Heaton[93] found styrene oxide, t-butyl alcohol, and water among the products of the reaction of t-butyl hydroperoxide with styrene, and assumed that decomposition of a hydroperoxide partly involves cleavage of the O–H bond:

$$ROOH + CH_2{=}CHR' \rightarrow R\dot{O}O + CH_2\dot{C}HR' .$$

When the polymerisation of isoprene is initiated with cumene hydroperoxide in heptane solution, the polymeric products are found to contain on the average one hydroxy-group per macromolecule[91], which confirms Denisov's scheme.

From the above results on the effect of solvents on the decomposition of hydroperoxides and hydrogen peroxide it can be seen that all solvents which accelerate the decomposition contain either heteroatoms having lone pairs of electrons or π-bonds: i.e. they are donors of electrons relative to hydroxy-groups. Some analogy is evident in the effect of solvents on the reactivity of radicals in reactions involving hydrogen atom abstraction, which have become known from the work of Russell[46], and in the decomposition of hydroperoxides. This analogy has a single cause—the diminution in the reactivity of radicals on complex formation with the solvent.

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The analysis which has been made of various radical reactions shows that the reactivity of radicals and molecules is considerably influenced by polar interactions of the reaction centre with substituents and with the medium. With few exceptions the reactivity of radicals is increased by the introduction of electron-acceptor substituents and by increase in the acidity of the medium or decrease in the electron-donor properties of the solvent. The opposite relations are observed for molecules.

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Institute of the Chemistry of Macromolecular Compounds, Kiev

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Condensation of Oxazoles with Dienophiles—a New Method for the Synthesis of Pyridine Bases

M.Ya.Karpeiskii and V.L.Florent'ev

The condensation of oxazoles with dienophiles is of the diene synthesis type, the final reaction products being substituted pyridine bases. The review deals with the literature data concerning the preparative applications of the condensation and the elucidation of the theoretical features of this process. In conclusion of the review, the application of heterodiene synthesis with participation of oxazoles in the preparation of vitamin B_6 and its analogues is discussed. The bibliography comprises 38 references.

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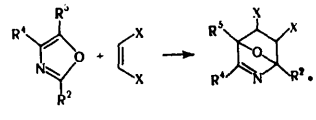
I. INTRODUCTION

Towards the end of the 1950's, Kondrat'eva [1,2] showed that the azadiene system of oxazoles readily reacts with an activated double bond by the diene synthesis mechanism [Diels–Alder mechanism (Ed. of Translation)]. The final products of this reaction are substituted pyridine bases. The reaction constitutes a very promising method for synthesising substituted pyridines including biologically important compounds—derivatives of nicotinic and isonicotinic acids, i.e. B_6 vitamins and their analogues.

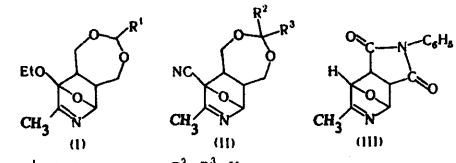
A series of papers have now been published on studies of the interaction between oxazoles and dienophiles both as regards the development of preparative methods for the synthesis of pyridine derivatives and the elucidation of the theoretical features of this interesting process. The synthesis of pyridine bases by the condensation of oxazoles with dienophiles consists of two stages. The first stage, the diene synthesis proper, results in the intermediate formation of bicyclic adducts:



Depending on the structure of the initial compound, the second stage can take place in several ways (see Scheme 1 and p. 37). Each of these stages has specific features and is of independent interest.

II. DIENE SYNTHESIS WITH PARTICIPATION OF OXAZOLES

The bicyclic adducts formed in the interaction between oxazoles and dienophiles are extremely unstable and usually cannot be isolated from the reaction mixture. Only three cases where the intermediate formation of the adducts has been rigorously established have been described. Thus in the reaction of 5-ethoxy-4-methyloxazole [3] and 5-cyano-4-methyloxazole [4,5] with substituted 4,7-dihydro-1,3-dioxepines. The racemates of the *endo*- and *exo*-isomers of compounds (I) and (II) were isolated:



(I) R^1 = H; iso-C_3H_7

(II) $R^2 = R^3 = H$; $R^2 = R^3 = CH_3$; R^2 = H; R^3 = iso-C_3H_7; R^2 = H; $R^3 = C_6H_5$

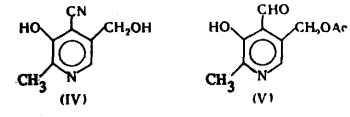
(III)

Similarly the condensation of 4-methyloxazole with *N*-phenylmaleimide yielded the adduct (III). [6] The stereochemistry of this compound was not studied.

As a result of the lability of the adducts produced in heterodiene synthesis, the characteristics of the individual reaction stages cannot be taken into account separately. Of the effects which should obtain mainly in the first stage of the heterodiene synthesis, it is necessary to consider in the first place the orientation of asymmetric dienophiles in the interaction with oxazoles.

In most cases the usual Diels–Alder reaction yields both possible isomers. In contrast, in heterodiene synthesis with participation of oxazoles only one of the products is formed as a rule. In her study of the interaction of alkyloxazoles with acrylic acid, Kondrat'eva [7] showed that this involves the formation exclusively of substituted isonicotinic acid and only in a few cases was it possible to detect traces of the second isomer–substituted nicotinic acid.

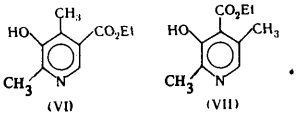
A similar observation was also made in the condensation of 5-ethoxy-4-methyloxazole with the nitrile of 4-hydroxycrotonic acid [8] and 4-acetoxycrotonic aldehyde [9]. Compounds (IV) and (V) respectively were isolated:



(IV) (V)

Thus, as a rule, the heterodiene synthesis takes place in such a way that the fifth position in the adduct is occupied by the most electronegative group of the dienophile.

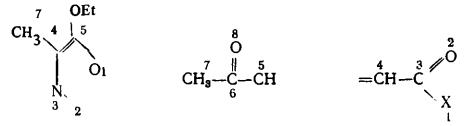
Exceptions to this rule were noted only with 4-methyloxazole. Thus in the reaction of this diene with ethyl crotonate the ester of 3-hydroxy-2,4-dimethylpyridine-5-carboxylic acid (VI) was obtained in 12% yield instead of the expected product (VII):[10]



(VI) (VII)

The sole attempt at a theoretical explanation of the first stage of the heterodiene synthesis was undertaken[11] in the study of the interaction between 5-ethoxy-4-methyloxazole and asymmetric dienophiles—β-acetylacrylic acid (VIIIa) and its ethyl ester (VIIIb). The authors[11] start with the hypothesis that the extreme polarisation of the azadiene oxazole system should favour reaction by a two-stage mechanism with separation of charges in the transition state. Then the orientation should be determined by the distribution of π-electron densities at the atoms participating in the transition state. To test this hypothesis, the parameters of the 5-ethoxy-4-methyloxazole molecule and its cation and also the anion and the ethyl ester of β-acetylacrylic acid were calculated. The calculations were performed by the LCAO-MO method in the Hückel approximation taking into account the effect of the hyperconjugation of the methyl group.

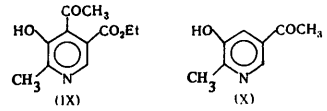
Distribution of π-electron densities



(VIIIa): X=O⁻
(VIIIb): X=OEt

Compound	q^{π} at different atoms							
	1	2	3	4	5	6	7	8
5-Ethoxy-4-methyloxazole	1.733	1.020	1.196	1.042	1.095	1.921	1.070	—
Cation of 5-ethoxy-4-methyloxazole	1.663	1.781	1.609	0.994	1.055	1.915	1.069	—
Ethyl β-acetylacrylate (VIIIb)	1.922	1.321	0.815	0.950	0.937	0.763	1.075	1.318
β-Acetylacrylate anion (VIIIa)	1.825	1.396	0.823	0.932	0.962	0.764	1.075	1.323

The Table shows that, in the product of the interaction of 5-ethoxy-4-methyloxazole with compound (VIIIb), the acetyl group must occupy the fourth position in the pyridine ring, while the opposite orientation should obtain in the reaction with the free acid (VIIIa), and the formation of substituted 5-acetylpyridine as the main product is to be expected. Indeed, after the condensation of 5-ethoxy-4-ethyloxazole with compound (VIIIb) only 4-acetyl-5-ethoxycarbonyl-3-hydroxy-2-methylpyridine (IX) was isolated, while in the condensation with compound (VIIIa) the only product obtained was 5-acetyl-3-hydroxy-2-methylpyridine (X).

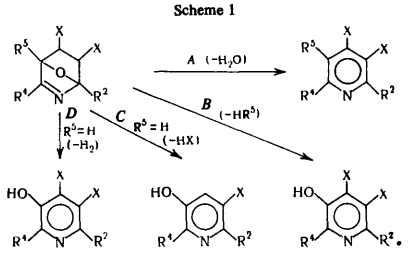


(IX) (X)

III. AROMATISATION OF THE ADDUCTS FROM DIENE SYNTHESIS

As already mentioned, the bicyclic adducts readily undergo aromatisation, particularly in acid media, and, depending on the structure of the starting compounds, the reaction can take place in four principal ways (Scheme 1).

Scheme 1

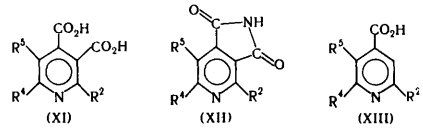


Usually all or several pathways operate simultaneously and heterodiene synthesis yields a more or less heterogeneous mixture of products. Analysis of literature data shows that the mode of aromatisation is determined by the nature of two substituents in the adduct—the substituent R^5 in the 4-position and the substituent X in the 5-position.

1. Aromatisation with Elimination of a Water Molecule (Kondrat'eva's Reaction)

The aromatisation of adducts via pathway *A* has been called Kondrat'eva's reaction. It resembles the aromatisation in acid media of the adducts obtained in the condensation of furan derivatives with dienophiles and usually takes place if the substituents R^5 and X in the adduct do not show a tendency to be eliminated in the form of anions.

Alkyloxazoles react in this way with maleic anhydride and maleic acid[2,12], forming alkyl-substituted cinchomeronic acids (XI); the reaction with maleimide[12-14] yields under these conditions the imides of cinchomeronic acids (XII) while the reaction with acrylic acid[7] gives analogues of isonicotinic acid (XIII):



(XI) (XII) (XIII)

where $R^2 = R^5$ = alkyl and R^4 = alkyl or aryl.

With other dienophiles, alkyloxazoles having an unsubstituted 5-position react via pathways *C* and *D* (see Section III, Subsection 3). Kondrat'eva[14] studied the behaviour in diene synthesis of oxazoles substituted in the 2- and 5-positions by electronegative groups. Dienes of this type do not react with maleic anhydride, but do react with maleimide via pathway *A*, forming normal products with yields lower by approximately 50% than for the corresponding alkyl-substituted oxazoles. Thus 2,4-dimethyloxazole gives the product (XII) in 93% yield, while with

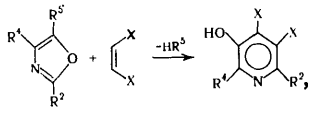
5-acetyl-4-methyl- and 5-ethoxycarbonyl-4-methyl-oxazoles, the yields of compound (XII) are 45 and 37% respectively.

The introduction of a phenyl group in the 4-position of oxazole has almost no effect on the interaction with dienophiles but 2- and 5-phenyloxazoles do not take part in heterodiene synthesis. On the basis of these data, the substituents of the oxazole ring can be arranged in the following sequence in terms of their effect on the reaction: alkyl ≃ 4-phenyl > $COCH_3$ > $COOC_2H_5$ ≫ 2- and 5-phenyl, the activity of oxazoles in the diene synthesis decreasing from left to right.

The occurrence of the reaction by pathway *A* is favoured when the diene synthesis is carried out in aprotic solvents. Japanese workers [12] have shown that the replacement of acetic acid by benzene in the reaction of 4-methyloxazoles with maleic anhydride leads to an increase of the yield of 2-methylcinchomeronic acid from 40 to 65%.

2. Aromatisation with Elimination of a Molecule of Alcohol or Hydrocyanic Acid

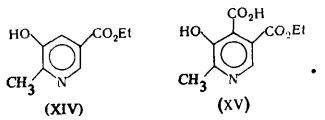
If a substituent which is readily eliminated in the form of an anion is present in the 4-position of the adduct, aromatisation takes place via pathway *B*, the final products being substituted 3-hydroxypyridines:



where R^5 = Oalkyl, $OCOOC_2H_5$, or CN. This reaction is characteristic of 5-hydroxyoxazoles with a protected hydroxy-group or of 5-cyanooxazoles.

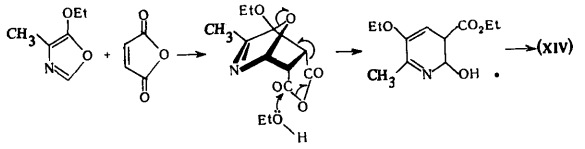
It is noteworthy that 5-alkoxyoxazoles, which are the most active dienes among oxazole derivatives, are comparable in their reactivity with carbocyclic dienes, the yields of the final products being usually high.

Firestone et al. [15], who studied the reaction of 5-ethoxy-4-methyloxazole with maleic acid anhydride in ether at 0°C, isolated 5-ethoxycarbonyl-3-hydroxy-2-methylpyridine (XIV) and the monoethyl ester of 3-hydroxy-2-methylpyridine-4,5-dicarboxylic acid (the main reaction product) after the aromatisation of the adduct with a solution of dry hydrogen chloride in absolute ethanol. The relative positions of the carboxy- and ethoxycarbonyl groups in the second product were not established rigorously, but the authors suggest the structure (XV) for this compound:



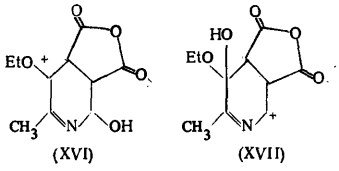
(XIV) (XV)

According to the authors, compound (XIV) is formed by the mechanism



Naito and Yoshikawa [6] did a lot of work on the determination of the composition of the reaction mixtures formed in the interaction between 5-ethoxy-4-methyloxazole and a number of dienophiles and showed that the main product is always accompanied by a certain amount (frequently traces) of a side product—3-hydroxypyridine with a free 4-position [a derivative of type (XIV)].

Firestone proposed two alternative mechanisms of the formation of the main product (XV) of heterodiene synthesis, differing in the position of the hydroxy-group and the localisation of the positive charge in the key intermediate (XVI) or (XVII). Both cations may arise in the heterolysis of the bonds of the oxygen bridge in the adduct by each of the possible pathways:

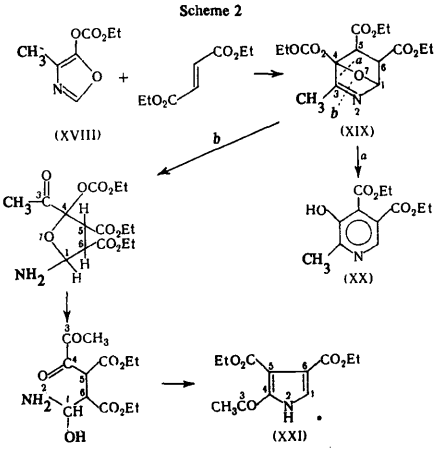


(XVI) (XVII)

Interesting results were obtained by Murakami et al. [16] in the study of the interaction of 5-ethoxycarbonyl-4-methyloxazole (XVIII) with diethyl fumarate (Scheme 2, below). The authors believe that, depending on the aromatisation conditions, the process may begin either with the dissociation of the C–O bond of the adduct (XIX), which leads to the diester of 3-hydroxycinchomeronic acid (XX), or with the dissociation of the C=N bond. In the latter case 2-acetyl-3,4-diethoxycarbonylpyrrole (XXI), the structure of which was demonstrated rigorously by proton magnetic resonance spectroscopy and by preparative synthesis, is obtained via a number of intermediates.

The particular pathway of the aromatisation of the adduct probably depends on the presence of water in the reaction mixture. Thus, by treating the adduct with a solution of dry hydrogen chloride in absolute ethanol, Murakami et al. [16] obtained 50% of the "normal" product (XX) and only 5% of the "anomalous" product (XXI), while treatment with concentrated hydrochloric acid gave the reverse proportions—5 and 54% respectively.

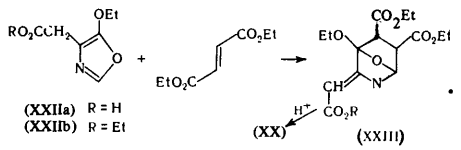
Scheme 2



(XVIII) (XIX) (XX) (XXI)

The above finding requires serious attention and further investigation in other instances of heterodiene synthesis via pathway *B*.

Miku and Matsuo [17] studied the interaction with dienophiles of 5-ethoxyoxazole-4-acetic acid (XXIIa) and its ethyl ester (XXIIb):



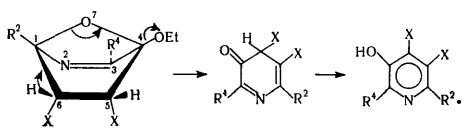
(XXIIa) R = H
(XXIIb) R = Et

The condensation of the ester (XXIIb) with diethyl fumarate leads, according to Miku and Matsuo [17], to the adduct (XXIII) with an exocyclic double bond. The structure of the latter was demonstrated by proton magnetic resonance and mass spectroscopy. The aromatisation of the adduct under the influence of acids is accompanied by the hydrolysis of the α'-ester group and the decarboxylation of the intermediate substituted pyridine-1-acetic acid, which is a β-imino-acid.

In the interaction of the free acid (XXIIa) with various dienophiles the aromatisation and decarboxylation take place directly during the reaction. Miku and Matsuo [17] do not associate this interesting phenomenon with the heterodiene synthesis but, referring to Doering and Pasternak [18], attribute it to the extremely ready decarboxylation of pyridine-1-acetic acids in an acid medium.

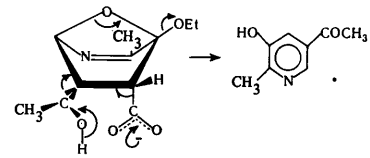
The following fact may be mentioned in connection with further consideration of the mechanism of the aromatisation of the adducts via pathway *B*: none of the investigators succeeded in isolating or demonstrating the presence in the reaction mixture of products corresponding to Kondrat'eva's reaction—substituted 3-alkoxypyridines.

The following mechanism was proposed for the adduct aromatisation stage [11]:



According to the authors the isomerisation of the adducts begins with the dissociation of the C^1–O bond. This conclusion is based on the following main postulates: (1) the C^1–O bond is in fact the one weakened to the greatest extent due to σ–π conjugation with the C^3=N bond. Under the isomerisation conditions (usually a solution of dry hydrogen chloride in alcohol), the heterolysis is favoured by the protonation of the adduct both at the nitrogen and at the oxygen atom; (2) the dissociation of the C^4–O bond with subsequent hydrolysis is unlikely if only because the diene synthesis and the isomerisation are most often carried out in complete absence of water. The validity of this hypothesis is confirmed by the examination of the diene synthesis with participation of 5-ethoxy-4-methylthiazole (see p. 544), the products of which are always 3-alkoxypyridines despite the fact that the aromatisation conditions (heating with concentrated hydrochloric acid) favour hydrolysis. (3) Finally, if the dissociation of the C^4–O bond is assumed, it is difficult to explain the exclusive formation of 3-hydroxypyridines in the interaction of dienophiles with 5-cyano-oxazoles.

In support of this mechanism, the authors quote the fact that the condensation of 5-ethoxy-4-methyloxazole with β-acetylacrylic acid is always accompanied by decarboxylation regardless of the reaction conditions, which results in the formation of 5-acetyl-3-hydroxy-2-methylpyridine:



Although the mechanism of heterodiene synthesis described above [11] is to a considerable degree speculative, it nevertheless accounts for the characteristics of this interesting reaction known at the present time.

As far as one can judge from the literature data, solvents do not have much effect on diene synthesis by the above mechanism. There is an indication [15] that small amounts of acids (for example, trifluoroacetic acid) catalyse heterodiene synthesis.

The reaction constitutes a very convenient method for the preparation of substituted 3-hydroxypyridines. The high reactivity of azadienes permits condensation with a wide range of dienophiles. Among the latter, the following compounds have been used: maleic anhydride [15,19], maleimide [19], esters of maleic and fumaric acids and fumaronitrile [9,15–17,20], 1,4-diacetoxy- and 1,4-dimethoxy-but-2-ene and 2,5-dihydrofuran [9,15,20–22], 2-substituted 4,7-dihydro-1,3-dioxepins [3,5], and a number of other compounds.

It is noteworthy that the limitations consisting in the low availability of the initial oxazoles which initially arrested the development of this method have now been to a large degree overcome as a result of a number of successful investigations of the synthesis of oxazoles [9,23–27].

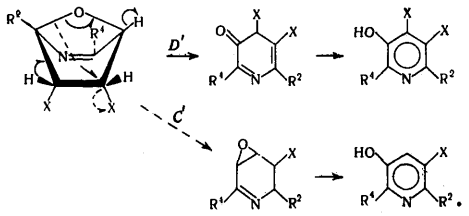
3. Other Pathways of the Aromatisation of Adducts

The aromatisation of adducts via pathways *C* and *D* is characteristic of the interaction of 5-unsubstituted oxazoles with dienophiles the substituents of which tend to be eliminated as anions. This type of aromatisation was investigated in the interaction of 4-methyl-, 4-phenyl-, and 2,4-dimethyl-oxazoles, with acrylonitrile [28], fumaronitrile and the diesters of maleic and fumaric acids [6,12], and a number of other dienophiles (see Scheme 1). As for pathway *B*, the final reaction product is 3-hydroxypyridine. In most cases both pathways operate simultaneously and, depending on the reaction conditions and the structure of the initial compounds, both products are obtained in various proportions.

We believe that the aromatisation of the adduct includes a stage in which the anion is displaced from the 3- or 4-position. This hypothesis is confirmed by the following findings. (1) According to the hypothesis, the reaction via pathway *C* should include the displacement from the 4-position of the substituent in the form of an anion, i.e. the substituent which previously belonged to the dienophile. Indeed, it has been shown [12] that, in the reaction of 4-methyloxazole with a series of dienophiles (fumaronitrile, acrylonitrile, diethyl fumarate, diethyl maleate, and ethyl acrylate), the yields of products via pathway *C* decrease from left to right in parallel with the capacity of the substituent of the dienophile to be eliminated as an anion. (2) The reaction via pathway *D* should include a stage in which an anion, i.e. a hydride ion, is displaced from the 3-position. Since this type of process is energetically unfavourable, the product of the reaction via pathway *D* is usually obtained in insignificant amounts, as an admixture to the product formed via pathway *C*. However, when the

reaction is carried out in the presence of hydride ion acceptors (hydrogen peroxide [12,29] or nitrobenzene at elevated temperatures [30]), pathway *D* becomes the main one and the yields of products reach 50–60%.

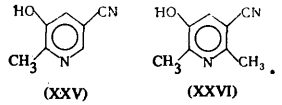
We believe that all these findings can be explained if it is postulated that the isomerisation of the adduct begins with the dissociation of the C^1–O bond of the oxygen bridge:



The liberated electron pair may attack either C^4 or C^5 atoms, displacing by a mechanism of the nucleophilic type either an X anion or a hydride ion.

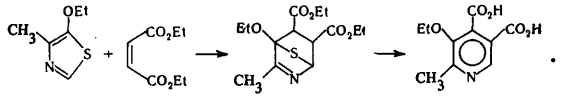
When the reaction is carried out in acid media, the yields of the products of heterodiene syntheses via pathway *C* are improved [1]. Thus, in the reaction of 4-methyloxazole with acrylonitrile [28] in benzene, 3-hydroxy-2-methylpyridine is obtained in 12% yield, while in acetic acid the yield is 28%.

The above pathway of heterodiene synthesis is not of particular value for synthetic purposes because of the low yields (usually 5–25%). An exception is the reaction of fumaronitrile with 4-methyloxazole [12,31] and 2,4-dimethyloxazole [6], which leads to substituted 5-cyano-3-hydroxypyridines (XXV) and (XXVI) in yields of 71 and 55% respectively:



(XXV) (XXVI)

In conclusion of the discussion of the diene synthesis of oxazoles, we shall describe the only study so far of the interaction with dienophiles of a derivative of thiazole—an oxazole heteroanalogue [32]. On heating for 8 h at 200°C with diethyl maleate, 5-ethoxy-4-methylthiazole (XXVII) forms the adduct (XXVIII), which undergoes aromatisation on heating with concentrated hydrochloric acid, hydrogen sulphide being eliminated:



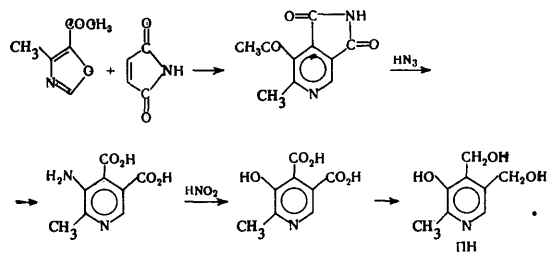
(XXVII) (XXVIII) (XXIX)

It is interesting to note that, in contrast to 5-alkoxyoxazoles, the isomerisation takes place in this case by a process of the type of Kondrat'eva's reaction and the final product is 3-ethoxy-2-methylpyridine-4,5-dicarboxylic acid (XXIX). The same product was obtained [32] by the reaction of compound (XXVII) with diethyl fumarate and maleic anhydride.

IV. APPLICATION OF HETERODIENE SYNTHESIS WITH PARTICIPATION OF OXAZOLES IN THE PREPARATION OF VITAMIN B_6 AND ITS ANALOGUES

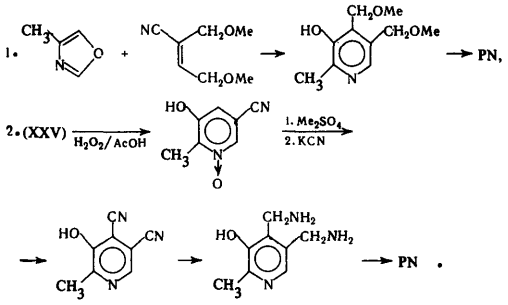
The interaction of oxazoles with dienophiles has been successfully used for the preparation of vitamin B_6 (pyridoxine) and its analogues. Methods for the synthesis of pyridoxine—3-hydroxy-4,5-bis(hydroxymethyl)-2-methylpyridine (PN) using heterodiene synthesis via pathways *A*, *B*, and *C* (Scheme 1) have been proposed. Kondrat'eva's reaction is not of great interest for the synthesis of pyridoxine, since the introduction of a hydroxy-group in the 3-position of the pyridine ring involves considerable difficulties. The sole attempt on these lines [33]—the synthesis of pyridoxine via Scheme 3—cannot be regarded as successful because of the complexity of the method and the low yields in the first two stages:

Scheme 3



In the series of pyridoxine analogues, this scheme can be used only to obtain products modified in the 3-position of the pyridine ring.

Two schemes based on heterodiene synthesis via pathway *C* have now been proposed for the synthesis of pyridoxine [10,34]:



The first synthesis is of exclusively theoretical interest, since the yield of 3-hydroxy-4,5-bis(methoxymethyl)-2-methylpyridine is very low. The second synthesis, despite the large number of stages, may find application in the synthesis of pyridoxine labelled at a carbon atom.

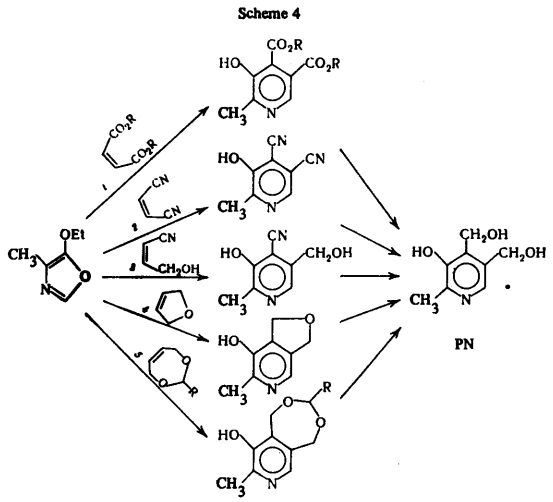
The most successful synthesis of pyridoxine and its analogues is heterodiene synthesis via pathway *B*. Its advantages include the following: high reactivity of 5-alkoxyoxazoles as dienes, high yields of final products, and simplicity. It is therefore not surprising that the efforts of investigators have been concentrated on the development of precisely this reaction (Scheme 4).

In syntheses *1–3* oxazole undergoes condensation with active dienophiles, which makes it possible to carry out the reaction under mild conditions (usually at 60–110°C). The yields of the final products amount to 75–86%. Further conversion of the compounds into pyridoxine does not present difficulties.

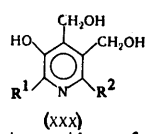
Since direct interaction of oxazole with but-2-ene-1,4-diol gives a low yield of pyridoxine, various butenediol derivatives have been used as dienophiles. Best results were obtained with 2,5-dihydrofuran [9,15,20–22] and 4,7-dihydro-1,3-dioxepine [3–5] (Scheme 4, pathways *4* and *5*). In this case the diene synthesis is carried out under more severe conditions than for pathways *1–3* (usually in an autoclave at 170–200°C) and the yields of the primary reaction products are somewhat lower (50–60%). However, the simplification of the process and the very high yields

of the final products give approximately the same yield of pyridoxine as in syntheses *1–3* of Scheme 4.

Scheme 4



The type of heterodiene synthesis considered above is very promising for the preparation of pyridoxine analogues. It makes it possible to modify virtually any position of the pyridine ring, with the exception of the third. A number of alkyl analogues of pyridoxine [compounds (XXXa)–(XXXf)] have been obtained by the interaction of 2- and 4-alkyl substituted 5-ethoxyoxazoles with diethyl maleate followed by the reduction of the esters of cinchomeronic acids with lithium aluminium hydride [35–38]:



(XXX)

a: $R^1=R^2=H$;
b: $R^1=H$; $R^2=CH_3$;
c: $R^1=R^2=CH_3$;
d: $R^1=C_2H_5$; $R^2=H$;
e: $R^1=$ iso-C_3H_7; $R^2=H$;
f: $R^1=$ n-C_4H_9; $R^2=H$.

Thus, the interaction of oxazoles with dienophiles constitutes a promising method for the synthesis of pyridine bases, in particular substituted 3-hydroxypyridines.

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During the preparation of the review for the press, a communication dealing with the condensation of 5-ethoxy-4-methyloxazole with *cis*- and *trans*-2,5-dimethoxy-2,5-dihydrofuran was published [39]. The authors isolated diene synthesis adducts and showed that the ratio of the *endo*- and *exo*-adducts is 2 : 1 in both cases. Aromatisation with an alcoholic solution of alkali gave 3-hydroxy-2-methylpyridine-4,5-dialdehyde.

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Institute of Molecular Biology,
USSR Academy of Sciences,
Moscow

Ion Exchange and the Swelling of Ion-exchange Resins

G.V.Samsonov and V.A.Pasechnik

The review deals with the modern hypotheses concerning the physicochemical properties of ion-exchange resins and their effects in the interaction between resins and solvents and solutes, mainly electrolytes. The problems associated with the permeability of resins, the steric accessibility of the functional centres, and their screening are discussed. Particular attention has been devoted to the interaction between resins and solvents. The thermodynamic conditions of such interaction (the changes in the integral and differential thermodynamic functions of swelling) have been elucidated. The isotherms for the absorption of water vapour have been discussed as a function of the content of the cross-linking agent, the ionic form of the resin, and the hydrophilicity of the matrix. In the section dealing with the comparison of the isotherms for the absorption of water vapour by resins with different degrees of cross-linking, attempts to describe them on the basis of osmotic concepts are discussed. The methods of the osmotic theory have been examined in detail: the characteristics of the hydration of ion-exchange resins which follow from the analysis of the differential and integral free energies of swelling and also from data derived by other methods, such as infrared and nuclear spin resonance spectroscopy. Certain model approaches to the study of the selectivity of ion exchange with participation of the solvent have been described. The thermodynamic methods for the analysis of the relation between the selectivity and swelling of resins are quoted.
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I. POROSITY, PERMEABILITY, AND SWELLING OF ION-EXCHANGE RESINS

Ion-exchange sorption and chromatography which originated on the basis of mineral and certain natural organic ion exchangers have assumed considerable importance following systematic studies on the synthesis of ion-exchange resins. The formation of a wide variety of cross-linked polymers containing acid or basic functional groups gave rise to insoluble acids, bases, and amphoteric compounds and salts capable of the absorption and exchange of various types of ions or the absorption of electrolytes from solutions. The possibility of modifying the structure of the matrix of a three-dimensional polymer and the properties and positions of acid–base groups and other active groups led to the creation of highly specific ion-exchange resins absorbing preferentially particular types of ions from solution. Ion exchange on resins takes place in heterogeneous systems incorporating a gel-like phase consisting of the grains of the swollen resin and the external solution. The capacity of the ions present in solution to reach all the functional groups in the resin and to exchange with the ions reversibly bound to the functional groups (counterions) is determined by the permeability of the gel phase of the resin grains to the ions undergoing sorption and desorption. Precisely in this sense one speaks of the porosity of the resin within the three-dimensional network or the microporosity, these terms being understood as the permeability to mobile ions. In the exchange of inorganic and organic ions of low molecular weight there is interaction with all the centres regardless of their positions in the bulk of the grains.

However, other cases are known where only part of the exchange centres are accessible to the ions absorbed. We encounter such phenomena in the absorption by resins of ions having large molecular weights, in particular organic ions[1,2]†. In the sorption of the triply charged streptomycin ions (M = 580 conventional units) on carboxylic acid resins, the exchange capacity of the sorbents is found to increase with the swelling coefficient, but the total ion exchange capacity of the resins with respect to metal ions cannot be attained. This phenomenon is attributed to the fact that the sorption of the streptomycin ion is accompanied by the screening of part of the exchange centres of the cation exchanger[4] because the dimensions of the organic ions exceed the average distance between adjacent functional groups. The same tendency is observed with the sextuply charged neomycin ions (mycerin, M = 720 conventional units): the sorption capacity increases with the swellability of the resins, but the total exchange capacity cannot be attained. When the sorbent grains are considerably comminuted, which usually leads to a sharp increase in capacity when the functional centres are sterically inaccessible, only a slight increase in the exchange capacity of the resin with respect to neomycin is noted. On the other hand, ion-exchange resins (even resins with relatively low swellability) with reduced exchange capacity absorb large organic ions at all the functional groups. Thus carboxy-phenolic resins with reduced exchange capacity sorb streptomycin and neomycin at all the functional centres regardless of the swelling coefficient[5].

A similar phenomenon was observed in the sorption of nucleotides on ion-exchange resins. The sorption capacity of Dowex-1 with respect to ATP, AMP, and UMP depends little on the content of the cross-linking agent in the resin and hardly changes over a certain range (1–8% of divinylbenzene).[6] It is much lower than the total exchange capacity of the resins with respect to small ions, i.e. a

†The phenomenon of the inaccessibility of part of the sorption centres to inorganic ions has been observed on zeolites[3].

large part of the active centres do not participate in the exchange processes. Partial deamination of the resin and the associated decrease of the total exchange capacity lead to a sharp increase of the relative exchange capacity with respect to the nucleotides. In the cases considered part of the exchange centres are screened, which makes them inaccessible to interaction with the ions in solution.

Another example of the dependence of the equilibrium properties of ion-exchange resins on their structure is the problem of the correspondence between ionic dimensions and the dimensions of the effective channels in which ions can migrate. This phenomenon is widespread and is sometimes called the phenomenon of ionic sieving (by analogy with molecular sieving in the separation of materials); it is revealed both in the dependence of the sorption capacity with respect to the given ion on the swellability of the resin and in the dependence of the sorption capacity of the given resin with respect to ions of different dimensions. Thus the sorption capacity with respect to singly charged cations of tetracycline antibiotics increases with the swellability of sulphonated resins and almost reaches the total exchange capacity with respect to metal ions (Fig. 1). Similar phenomena occur also in anion exchange.

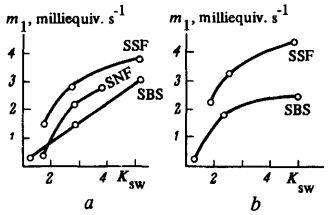

Figure 1. Dependence of the absorption capacity of sulphonated resins with respect to aureomycin (a) and terramycin (b) on resin swellability; K_{SW}—the swelling coefficient in the initial ionic form.

On increase in the swelling coefficients of anion exchangers, there is an increase in the sorption capacity with respect to the singly charged penicilin ion (M = 244 conventional units).[7] The dependence of the sorption capacity with respect to the singly charged novobiocin anion (M = 612 conventional units) on the swelling coefficient of the FAF resin is also described by an S-shaped curve. Screening of part of the sorption centres in the sorption of large organic ions and the inaccessibility of the sorption centres cannot be always unambiguously distinguished. The problem of the correspondence of the physicochemical properties of ion-exchange resins and the characteristics of the chemical and steric structures covers a wide range of phenomena and is one of the central problems in the theory of ion exchange. The solution of this problem involves the determination of quantitative relations between the properties of the initial components of the reaction mixture and those of the copolymers formed under the chosen conditions. At the present time the problem cannot be solved in a general form, although parts of it are susceptible to quantitative studies. The principal feature of the problem is the hypothesis of channels or pores through which the substances sorbed by the resin migrate. There exist ion-exchange materials, for example mineral and synthetic zeolites, which have channels which are homogeneous with respect to size and regular in shape. Zeolites are aluminosilicates and the characteristics of their structure are associated with the tetrahedral coordination of oxygen around aluminium and silicon and also the strength of the bonds between these elements and oxygen. In cross-linked organic polyelectrolytes such homogeneity of the channels cannot be achieved because of the different reactivities of the monomers, their complex dependence on the conversion, and also the possibility of various orientations of the polymer chains as a result of the rotation of methyl and other groups. The channels along which sorption of substances by ion-exchange resins takes place cannot be characterised in detail. Average characteristics such as porosity and permeability have been adopted for their description. The porosity P is the fraction of the volume of the resin grain occupied by pores, i.e.

$$P = \frac{v_1}{v_2},$$

where v_1 and v_2 are the pore volume and the total volume of the resin grain. For some resins, v_1 and v_2 change relatively little on hydration‡. The porosity of such resins has been called the intrinsic porosity.

Swelling resins can also be characterised by the porosity P, but the latter is not a constant. In the dry state $P \simeq 0$ and in the swollen state it can be extremely high and can exceed the value of P for intrinsically porous ion-exchange resins. This porosity has been called the latent porosity. The concept of "permeability" has been introduced in the study of liquid flow through membranes and filters formed from finely disperse materials. In this case the permeability is characterised by the permeability coefficient which enters into D'Arcy's linear filtration law. The permeability of ion-exchange resin grains cannot be defined in this simple form due to the lack of an evident analogy with the phenomenon of liquid flow and the complexity of the conditions in which the diffusion of substances absorbed takes place. Therefore it is now usual to speak of the permeability of disperse ion-exchange materials in the sense that it characterises their capacity to absorb substances. A measure of the permeability of an ion-exchange resin is the amount of substance absorbed under the given conditions. Thus porosity characterises mainly the sorbent, while permeability characterises its interaction with the medium§. The permeability of ion-exchange resins depends on the type of substance absorbed. Therefore the permeability to the solvent, for example, may differ from the permeability to ions. The permeability of ion exchangers depends on the amount of cross-linking agent and its nature. Thus when 20% of divinylbenzene is used in the synthesis of KU-2 sulphonated styrene resin, the product has a swelling coefficient of 1.3–1.4. A similar low swellability of the analogous SBS sulphonated styrene resin is achieved by the introduction of 70% of butadiene (divinyl). Three cross-linking agents

‡Ion-exchange resins may be hydrated both without a significant change in grain volume (resins with a large content of the cross-linking agent, macroporous resin) and with a considerable change in this volume. In the latter case hydration is frequently referred to as swelling. In the literature on ion exchange the term "swelling" is used as a synonym for "hydration".

§In resins with latent porosity the porosity and permeability characterise only the interaction between the resin and the medium.

are most widely used: divinylbenzene (*o*-, *m*-, and *p*-isomers), butadiene, and triazine. A copolymer with the most regular structure is formed when one of the pure isomers of divinylbenzene is used as the cross-linking agent. We believe that ion exchangers with butadiene or triazine as cross-linking agents have a less regular structure [8].

Table 1. Physicochemical methods for the investigation of the structure of ion-exchange resins.

Method	Object of study	References
Application of the theory of capillary condensation	Dowex-50 in H^+-form	9
	KB-4 in H^+-form	10
	macronetwork carboxylic acid resins in H^+-form	10
Measurement of the steric accessibility of functional centres to organic ions with increase in their dimensions	KMT, KB-4, KFU, KFUh	2
	macroporous resins	2
	Wofatit	11
	Amberlyst 1R-45	12
	Levatit MII	12
	SBS, KU-2, Permutit	2
	KRS, KRF	13
Depression of the freezing point of the solvent in resins	phenolsulphonic acid resin	14
Determination of the specific absorbing surface by BET method, the porosity, and the average pore diameter	macronetwork resins	10
	macroporous resins	15
	SG-1, AN-2F, EDE-10P, AV-17	15
	skeletons of macroporous resins	16
	macroporous resins	15
Determination of microhardness	SG-1 x 5, AN-2F	17
Electron microscope method	Dowex-50 resins	18
	macroporous resins	19
X-Ray diffraction	Amberlyst 15	20
	KU-1, KU-2, KB4P2	21
Microradiographic study of resin sections	AN-2F, SG-1	17
Optical properties in transmitted and reflected polarised light beams	Carboxylic acid resins	17
	DK-3, DKR, SG-1TS, SG-1P x 5, SG-1 x 5	
Absorption spectra in the visible region	resins saturated with dyes	22, 23
Reflection spectra in the visible region	metal complexes with carboxylic and sulphonic acid cation exchangers	24, 25
Ultraviolet spectroscopy	phenolsulphonic acid, polyethylene-polyamine, and styrene resins	26, 27
Infrared spectroscopy	water in resins	28-31
	structure of styrene resins	32-34
Nuclear magnetic resonance	structure of water in styrene resins	33, 35-39
	anion exchangers in F^--form	40, 41
Electron spin resonance	cation exchangers in Cr- and Mn-forms	42-44
Measurement of magnetic susceptibility	cation exchangers in Fe-form	45
	anion exchangers in OH^-- and Cl^--forms	46
	resins with complex cations and anions	47

The number and relative positions of the functional centres have a significant influence on the permeability of resins. This phenomenon was discussed above (see p. 1257).in connection with the problem of the inaccessibility and screening of functional centres. Numerous methods developed earlier for mineral sorbents are used to estimate the permeability and porosity of ion-exchange resins. Mineral sorbents are in most cases intrinsically porous and their porosity can be investigated both in the dry state and in the presence of a solvent in the pores. A similar approach is unfortunately inapplicable to all types of ion-exchange resins, since, on swelling of resins with latent porosity, the permeability changes. To investigate the structure of ion-exchange resins, it is best to use methods which permit the estimation of the dimensions of the "expanded" regions between three-dimensional networks in the presence of maximum swelling of the resins, since it is then possible to compare the results with those for their permeability under ordinary conditions. It is noteworthy that none of the methods employed at present to estimate the porosity or permeability of resins is absolute. The choice of a particular method depends both on the characteristics of the given problem and on the individual characteristics of the sorbents. Various methods for the investigation of the structure of ion-exchange resins are listed in Table 1 and have been described in a number of reviews [4,74].

Figure 2 presents graphical models of ion-exchange sorbents with different porosities and permeabilities. Until recently the structural type A, characterised by an alternation of expanded and contracted regions in the polymer network, was most widely used. It should be noted that we are dealing with swelling ion-exchange resins and therefore structure A represents the state of the resin containing a solvent. When the latter is removed, the polymer chains close up and the differences between regions with different cross-linking densities are to a large degree smoothed out. In the dry state the packing density of the polymer chains is such that the resin hardly absorbs neutral gas molecules (see Table 2).

In the swollen state ion exchangers of this type are characterised by considerable intramolecular permeability. Almost all their functional centres are accessible to inorganic ions. However, when the degree of cross-linking of resins increases, the functional groups may become screened and sterically inaccessible. A steric model of the styrene–divinylbenzene cation-exchange resin of this structural type was proposed by Grubhofer [18].

If x is the molar percentage of the cross-linking agent (divinylbenzene), then the number of ethylene groups per

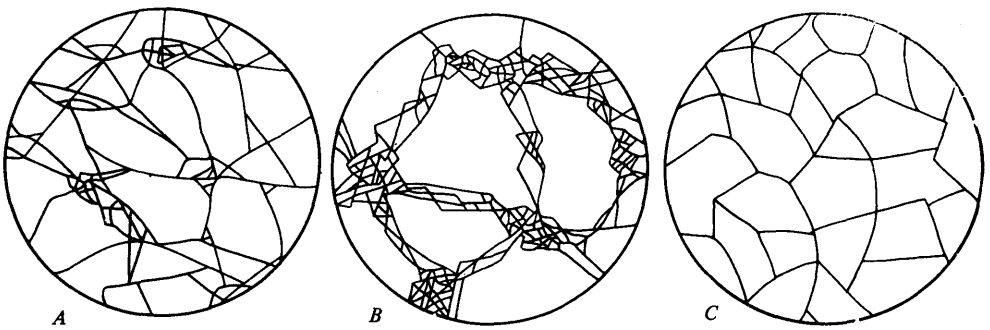

Figure 2. Graphical models of resins of different structural types: A) resin of Dowex-50 type; B) macroporous resin; C) macronetwork resin.

cross-link between the points of attachment of the latter is $y = \frac{1}{2}(100/x + 1)$. The distance between two branching points in the network [taking into account the thickness of the benzene ring (4.5 Å), the length of two carbon–carbon bonds in the phenyl group (2×1.5 Å), and the size of a single monomer unit (2.2 Å)] is

$$a(\text{Å}) = 2.2y + 7.5.$$

Table 2. Internal surfaces of various sorbents.

Sorbent	Form of sorbent	$\bar{d}$, nm	Area of channels, $m^2 g^{-1}$	Refs.
CaA zeolite	Ca		1640	48
NaX zeolite	Na		1400	48
Silica gel	—		507	49
Macroporous resins:				
Amberlyst 15	Na		42.5	50
Amberlyst XN-1001	Cl		62.9	50
KR-1	Pb, Cr	300	3.0	19
KR-2	Pb, Cr	79	31.0	19
AR-1	$PtCl_6$	160	3.2	19
Ordinary resins:				
Amberlyst IR-120	Na		0.1	50
Amberlyst IRA-400	Cl		0.1	50
Macronetwork resins:				
Carboxylic acid cation exchanger	H, Na		<0.1	10, 5
Sulphonic acid cation exchanger	H, Na		<0.1	10, 5

The angle between the main chain and the cross-link is assumed to be 90°. To obtain the dimensions of the cell accessible to the diffusion of ions, it is necessary to subtract from the resulting cell diameter the thickness of the polystyrene chain, i.e. 15 Å. Grubhofer's results for a high content of cross-linking agents in resins agree well with independent estimates of their cell dimensions, and for low contents of the cross-linking agents they agree with data obtained by the electron microscope study of the same specimens in the dry state. This shows that the model describes correctly the fundamental structural characteristics of resins based on styrene and divinylbenzene, despite the fact that it is undoubtedly a very rough approximation, disregarding a whole series of phenomena which obtain in the formation of copolymer structures (the presence of amorphous regions, non-uniform sulphonation, intertwining of chains, etc.).

An unusual type of porosity arises in the synthesis of resins where an inert component (including polymers) is used in the copolymerisation process [52–55]. Resins of this type are called macroporous. They are distinguished by a considerable heterogeneity of structure and are characterised by the presence of regions with higher and lower matrix densities (Fig. 2*B*). The macroporosity of a resin differs significantly from the permeability within the three-dimensional network. The channels in a macroporous sorbent, which have a large internal area, exist also in the unswollen polymer (Table 2). Such channels are absent from ordinary ion-exchange resins. Comparison of the structures of macroporous and ordinary resins with maximum moisture content shows that in the first case there are pores whose dimensions are several times greater than the "expanded" regions between the networks in ordinary resins. When macroporous resins are hydrated, their degree of swelling changes insignificantly. Owing to regions with high matrix density, macroporous resins are distinguished by considerable mechanical strength. The porosity of resins of this type may be characterised as intrinsic porosity.

Certain physicochemical characteristics of the resins are given in Table 2. KR-2 cation-exchange resin was obtained using additives of lower molecular weight than for KR-1 cation exchanger, as a result of which it has a higher surface area, but the average dimensions of its pores are smaller.

It is interesting that cases intermediate between macroporous and ordinary resins are possible; these resins are characterised by latent porosity. Thus AR-1 anion-exchange resin exhibits all the features of a macroporous resin and yet is capable of swelling. Electron diffraction shows that the structures of macroporous resins consist of agglomerates of quasispherical particles with interconnecting cavities between them. The microspherical particles of macroporous resins consist of a gel similar in properties to the gel of ordinary resins, but containing a much higher amount of the cross-linking agent and consequently having a much higher matrix density. The active centres can be located both on the surface of the microspherical particles and within them. Therefore diffusion coefficients measured in macroporous resins are a result of the superposition of the diffusion of ions in the system of cavities and in the gel of the microspherical particles. Similarly the absorption of a solvent by macroporous resins must be regarded as occurring both in the microspherical particles and in the spaces between them. Kunin [56] showed that the absorption of a solvent by macroporous resins takes place in two stages. Initially the microspheres are hydrated and then the spaces between them are filled, the fraction taken up by the microspheres in the cases which he investigated amounting to 28–30% of the total amount of the solvent absorbed. Experimental proof of the occurrence of this phenomenon is provided by the dependence of the amount of mercury which can be forced into the resin on the content of the solvent $\bar{n}_W$. Up to a certain value of $\bar{n}_W$, the porosity either does not change or increases somewhat, but, after the attainment of a critical value, it falls sharply. Evidently a significant cause of the decrease of the porosity is the end of the hydration and swelling of the microspherical particles and the appearance of the solvent between them. The results of experiments in which mercury is forced into the resin also show that the pore dimensions change in the swelling of macroporous resins: large pores become still larger and smaller pores decrease further in size. This phenomenon may be explained by the competition between the processes involving the swelling of the microspherical particles and their deformation on swelling.

The microspherical particles in macroporous resins may be regarded as having latent porosity. In the exchange of small inorganic ions all the functional centres of macroporous resins are accessible. With organic ions, the permeability falls sharply. This may be attributed to the steric inaccessibility to organic ions of the functional centres within the bulk of the microspherical particles and the accessibility of those on the surface of the particles. The phenomenon of steric inaccessibility to tetraethylammonium, triethylbenzylammonium, Methylene Blue, and Crystal Violet ions has been observed in macroporous ion-exchange resins where the capacity due to the functional centres on the surface of microporous particles amounted to 40–50% of the capacity with respect to inorganic ions. On further increase of ionic size, the permeability of the resin changes relatively little [2]. The presence of heterogeneous regions is reflected also in the kinetic properties of macroporous resins. When the functional centres of the microspherical particles are sterically inaccessible, the diffusion coefficient is determined solely by the dimensions

of the macropores. Thus the diffusion coefficients of the ions of quaternary ammonium bases in the macroporous KU-2 resin depend little on the dimensions of the ions in the series tetramethylammonium–triethylbenzylammonium. On the other hand, for ordinary resins of a similar type the rates of diffusion within the same group of ions decrease significantly with increase in their size.

A number of papers have been published recently on the methods of synthesis and the properties of new types of resins with enhanced permeability. Thus, when a telogen is used as a diluent, there is a possibility of breaks in the main chain [57]. The permeability of resins of this kind is higher due to the formation of "defects" in the main chain and due to the dilution of the monomer mixture. A method has been developed for the synthesis of sulphonic acid and carboxylic acid cation exchangers with larger dimensions of the interchain spaces as a result of the use of cross-linking agents with different chain lengths. *NN'*-Alkylenedimethacrylamides proved to be suitable for this purpose [4,10,58-60]. The elementary unit of KMDM macronetwork resins has the following structure.

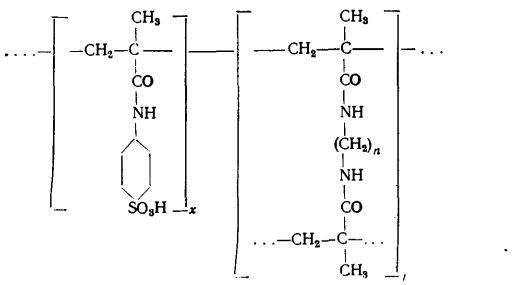

Table 3. Mutual diffusion coefficients of Methylene Blue and streptomycin ions in resins.

Sorption of Methylene Blue on KU-2 sulphonic acid resin (H^+-form, 40°C)		Sorption of streptomycin on KMDM-6* carboxylic acid resin (Na^+-form, 20°C)	
degree of saturation F	diffusion coefficient $10^{10}D$, $cm^2 s^{-1}$	degree of saturation F	diffusion coefficient 10^7D, $cm^2 s^{-1}$
0	1.7	0.23	1.1
0.13	1.6	0.35	1.1
0.40	0.5	0.51	1.3
0.62	0.25	0.86	1.3
0.80	0.35	0.95	1.2

*Cross-linking agent—hexamethylenedimethacrylamide.

The permeability of such resins may be altered both by changing the content of the cross-linking agent and by changing the length of its chain. Macronetwork resins probably have a structure of type *C* (Fig. 2), which is called isoporous. With suitable "pore" dimensions in these resins, there is a possibility in the latter only of the screening of functional centres. The high permeability of such resins to organic ions is reflected, in particular, in their capacity to sorb rapidly ions of large molecular weight. The diffusion coefficient of streptomycin ions in the grains of this resin is not only very high but also it does not decrease during the sorption process (Table 3).

Until recently it was suggested that a cross-linking three-dimensional polyelectrolyte capable of swelling may be regarded as a system with highly elastic properties in which thermal density fluctuations take place [61]. On this basis, the hypothesis was put forward that the incorporation of ions into the grains of the swollen resins may be associated not only with the presence of permanent pores of channels but also with the presence of fluctuating expanded regions in the polymer network. Then the conformational properties of the polymer network can be calculated on the basis of Flory's theory of polymer solutions, one of the results of which is a decrease of the entropy of the network on swelling. However, in a study of the thermodynamics of the exchange of quaternary ammonium ions for Na^+ ions on cross-linked sulphonated polystyrene resins (containing 8% of divinylbenzene), Boyd and Larson [62] observed that, when the resin is converted into the quaternary ammonium-form, its volume increases but the network entropy increases also instead of decreasing. The study of the elastic characteristics of films of sulphonated phenol–formaldehyde resins also showed [63] that the entropy of their extension is positive. These experimental findings and also the value of Young's modulus of ion-exchange resins, which is 10^8–10^9 dyn cm^{-2}, i.e. higher by a factor of ten than the value of Young's modulus of rubbers, led to the conclusion [64] that ion-exchange resins of certain types behave as if they were polymers in the vitreous state. Then one may expect that the mobility of the polymer network is fairly low and network density fluctuations under the influence of thermal motion cannot lead to significant changes in the shape of the "pores".

II. INTERACTION OF ION-EXCHANGE RESINS WITH SOLVENTS

a. Methods for the Investigation of the Interaction of Ion-Exchange Resins with Solvents

The study of the solvation of ion-exchange resins¶ is important both for the investigation of their physicochemical properties (structure, amount of cross-linking agents, hydrophilicity of the fixed groups and counterions, etc.) and for the elucidation of the mechanism of ion exchange. A quantitative characteristic of the interaction of the resin with a solvent is provided by the isotherms for the adsorption of the latter from the vapour phase or from solution (the so called isopiestic lines). Isopiestic lines are usually measured in the vapour pressure range from negligibly low values up to the vapour pressure (p_0) of the pure solvent ($0 \leq p/p_0 = \alpha \leq 1$). The temperature coefficients of isopiestic lines over the entire range of values of α are also important. The composition of the vapour phase is regulated by solutions of salts [65,66] or sulphuric acid [67], the water vapour pressure above which is known over a wide range of temperatures and concentrations. On the basis of the isopiestic lines and their temperature coefficients (or on the basis of the heats of hydration), it is possible to calculate all the thermodynamic functions characterising the interaction of the resin with the solvent. The application of the thermodynamic method to resins [68,69] has developed largely by analogy with the thermodynamics of the hydration of natural macromolecular compounds [70,71].

Suppose that we have a resin with a specified ionic composition containing a certain amount of absorbed solvent

¶We shall consider only the interaction with water.

$\bar{n}_{1w}$ moles per equivalent of ions) in equilibrium with the vapour of the latter whose pressure is p_1. If the pressure changes, for example increases, there is a corresponding change also in the equilibrium content of the solvent in the resin. The increase in moisture content in the process where sorption does not alter the equilibrium vapour pressure may be represented by the following equation:

$$n_i[\bar{n}_{1w}(p_1)] + n_w(p_2) \rightarrow n_i[\bar{n}_{1w} + \bar{n}_w, (p_2)], \quad (1)$$

where n_i is the amount of ion-exchange resin (in grammes) containing E equivalents of exchange centres and $n_w(p_2) = \bar{n}_w(p_2)$.

The increment of the Gibbs free energy of the system during process (1) is

$$\Phi_{sw} = n_i[\mu_i(p_2) - \mu_i(p_1)] + \bar{n}_{1w}[\bar{\mu}_w(p_2) - \bar{\mu}_w(p_1)] = n_i\Delta\mu_i(p_2, p_1) + \bar{n}_{1w}RT\ln\frac{p_2}{p_1}, \quad (2)$$

where Φ_{sw} is the free energy of swelling in process (1) and $\bar{\mu}_w(p_2) = \mu_w(p_2)$. The change in the composition of the vapour phase may be neglected in the derivation of Eqn. (2), because swelling can always be studied under conditions such that the change in the number of moles of water in the vapour phase is very small, with a small resin sample, or under conditions such that this change is compensated by the evaporation of part of the solvent from the electrolyte maintaining the given vapour pressure. The change in the free energy of the vapour is then zero (at T = const. and p = const.) and therefore makes no thermodynamic contribution to the swelling process. On the other hand, the Gibbs–Duhem equation applies to the equilibrium system (at a pressure p_2):

$$n_i d\mu_i + (\bar{n}_{1w} + \bar{n}_w)\, d\bar{\mu}_w = 0, \quad (3)$$

$$d\mu_i = -\frac{(\bar{n}_{1w} + \bar{n}_w)}{n_i}\, d\bar{\mu}_w. \quad (4)$$

According to Eqn. (4), the change in the chemical potential of the ion-exchange resin when the equilibrium vapour pressure changes from p_1 to p_2 is

$$\mu_i(p_2) = \mu_i(p_1) = -\int_{\mu_w(p_1)}^{\mu_w(p_2)} \frac{(\bar{n}_{1w} + \bar{n}_w)}{n_i}\, d\mu_w. \quad (5)$$

Since $\bar{n}_{1w}$ is independent of the pressure p_2, it follows that

$$\mu_i(p_2) - \mu_i(p_1) = -\frac{\bar{n}_{1w}}{n_i}RT\ln\frac{p_2}{p_1} - \int_{\bar{\mu}_w(p_1)}^{\bar{\mu}_w(p_2)} \frac{\bar{n}_w}{n_i}\, d\mu_w.$$

On substituting the change in the chemical potential of the resin determined from Eqn. (6) in Eqn. (2), we obtain

$$\Phi_{sw} = -\int_{\ln\alpha_1}^{\ln\alpha_2} \bar{n}_w RT\, d\ln\alpha, \quad (7)$$

where $\alpha = p/p_0$ and p_0 is the vapour pressure of the pure solvent. To facilitate the comparison of the free energies of swelling of various resins, it is necessary to select standard states for the resin and solvent vapour; usually one chooses the dry resin and the vapour over the pure solvent ($p = p_0$). Then swelling is measured from the state where $p_1 = 0$. The free energy of the transfer of n_w moles of the solvent from the vapour at a pressure p_0 to the vapour at a pressure p_2 is

$$\Phi_{sw_2} = n_w[\mu_w(p_2) - \mu_w(p_0)] = n_w RT\ln\alpha. \quad (8)$$

Thus the change in the free energy of swelling of the resin from the chosen standard states to the specified mixed state is

$$\Phi_{sw} = \Phi_{sw_1} + \Phi_{sw_2} = \bar{n}_w RT\ln\alpha - RT\int_0^{\alpha} \bar{n}_w\, d\ln\alpha = RT\int_0^{n_w} \ln\alpha\, dn_w. \quad (9)$$

We may note that the value of Φ_{SW} calculated by Eqn. (9) corresponds to a hypothetical swelling process where in the equilibration of the dry resin ($p = 0$) with the vapour of the pure solvent ($p = p_0$) the equilibrium vapour pressure decreases to $p_2 > p_0$. Φ_{SW_1} corresponds to the process in a humidifier where p_2 = const. Eqn. (9) thus corresponds to the following free energy difference [68,69]:

$$\Phi_{sw} = \bar{n}_w\bar{\mu}_w(p_2) + n_i\mu_i(p_2) - n_w\mu_w(p_0) - n_i\mu_i(p=0) = \bar{n}_w[\bar{\mu}_w(p_2) - \mu_w(p_0)] + n_i[\mu_i(p_2) - \mu_i(p=0)]. \quad (10)$$

Comparison of Eqns. (9) and (10) shows that the first term in the former characterises the change in the state of the solvent and the second the change in the state of the resin during the sorption process. Similar equations can be written also for the heat of sorption [assuming that $\bar{h}_w(p_2) = h_w(p_2)$]:

$$H_{sw} = \bar{n}_w[\bar{h}_w(p_2) - h_w(p_0)] + n_i[h_i(p_2) - h_i(p=0)], \quad (11)$$

where $\bar{h}_w$ and h_i are the partial heats of sorption of the solvent and of the swelling of the resin. The partial quantities referring to the solvent can be found in the following way:

$$\bar{h}_w(p_2) - h_w(p_0) = \frac{\partial\left(\frac{H_{sw}}{n_i}\right)}{\partial\left(\frac{\bar{n}_w}{n_i}\right)}. \quad (12)$$

On combining Eqns. (11) and (12), we obtain the difference between the partial heats $h_i(p_2) - h_i(p=0)$ characterising the swelling of the resin:

$$h_i(p_2) - h_i(p=0) = \frac{H_{sw}}{n_i} - \frac{\bar{n}_w}{n_i}\cdot\frac{\partial\left(\frac{H_{sw}}{n_i}\right)}{\partial\left(\frac{\bar{n}_w}{n_i}\right)} = -n_e^2\frac{\partial\left(\frac{H_e}{n_e}\right)}{\partial n_e}, \quad (13)$$

where $\bar{n}_e = \bar{n}_w/n_i$ is the equivalent moisture content of the resin and $H_e = H_{SW}/n_i$ the equivalent heat of sorption of the solvent.

Subdivision of the experimental heat of sorption of the solvent into components associated with the change in the thermodynamic state of the resin (the matrix or the ions and counterions fixed on the matrix) and the solvent permits the estimation of their relative contributions and thereby provides quantitative data for the elucidation of the thermodynamic effects of the swelling process. Additional information can also be obtained by comparing the changes in the Gibbs free energies and enthalpies of swelling:

$$\bar{\mu}_w(p_2) - \mu_w(p_0) = \bar{h}_w(p_2) - h_w(p_0) - T[\bar{S}_w(p_2) - S_w(p_0)], \quad (14)$$
$$\mu_i(p_2) - \mu_i(p_0) = h_i(p_2) - h_i(p_0) - T[S_i(p_2) - S_i(p_0)].$$

Eqns. (14) and (15) permit the determination of the partial entropies of sorption of the solvent and of swelling of the resin ($\bar{S}_w$, S_i). The determination of the partial thermodynamic quantities of Eqns. (12)–(15) is possible when the heats of sorption are measured together with the sorption isotherms of the solvent [frequently called "isopiestic" lines, the term reflecting the sorption mechanism defined by Eqn. (1), since the vapour pressure then remains unchanged]. Calorimetric determination of the heat of sorption of the solvent is most advantageous, since

it is then possible to obtain the most accurate values of the enthalpy of swelling as a function of the equilibrium amount of solvent absorbed. From the experimental standpoint, the following procedure for the determination of this function is convenient. Initially it is necessary to measure the integral heat of sorption when the dry resin is mixed with an excess of the solvent. Then the resin is equilibrated with the vapour of the solvent and the heat of mixing with an excess of the solvent is determined for this state. The difference between the two heats represents the heat of conversion of the dry resin into the partially hydrated state corresponding to the chosen vapour pressure. By varying the equilibrium vapour pressure, it is possible to obtain a curve relating H_{SW} to the content of the solvent in the resin. However, this relation can also be calculated provided that the isopiestic lines for the given resin are available at several temperatures. It is known that the heat of a chemical reaction which is independent of temperature (if it does vary with temperature, then the average heat in the given temperature range is employed) may be calculated from the temperature variation of the Gibbs free energy:

$$H_{sw} = -T^2 \frac{\partial \frac{\Phi_{sw}}{T}}{\partial T} \qquad (16)$$

When the temperature changes, the free energy of swelling changes too, since this involves a change in the content of the solvent in the resin. For further discussion, it is convenient to introduce the concept of the isosteric heat change H_{is}, i.e. the heat change occurring when the solvent is redistributed between the resin and the vapour on changing the temperature but the total amount of solvent remains constant:

$$H_{is} = -T^2 \frac{\partial^2}{\partial T\, \partial \bar{n}_w} \left[\frac{\Phi_{sw}}{T}\right] . \qquad (17)$$

It is easy to show that

$$H_{is} = \left.\frac{\partial H_{sw}}{\partial \bar{n}_w}\right|_{T,p} . \qquad (18)$$

The isosteric heat change can be conveniently determined from two isopiestic lines corresponding to different temperatures on the basis of the following equation:

$$H_{is} = \frac{RT_1T_2}{T_2 - T_1} \ln \left.\frac{\alpha_1}{\alpha_2}\right|_{\bar{n}_w} , \qquad (19)$$

where $T_2 > T_1$ and α_2 corresponds to the temperature T_2. If H_{is} is determined for different values of $\bar{n}_w$, then the integral heat of sorption H_{SW} may be determined as follows [see Eqn. (18)]:

$$H_{sw} = \int_0^{\bar{n}_w} H_{is}\, d\bar{n}_w . \qquad (20)$$

The calculation of H_{SW} by Eqns. (16) and (20) should in principle yield the same enthalpies of swelling, but in the second case the results are more accurate, since there is an additional computational operation in Eqn. (16) involving integration.

The change in the solvent content of the resin with temperature in the range of several tens of degrees is small, which of course leads to a low accuracy in the determination of the enthalpy of swelling from the temperature variation of Φ_{SW}. In consequence of the condition $\bar{n}_w$ = const., H_{SW} can be calculated down to the smallest swellability in the given temperature range (as a rule it corresponds to the highest temperature).

Together with the development of thermodynamic techniques for the investigation of ion-exchange resin solvation, physical methods are being increasingly employed at the present time: NMR and infrared spectroscopy, methods based on the study of the dielectric properties of the resins, etc. The principal conclusions arrived at on the basis of these methods are described below.

b. Characteristics of the Interaction of Ion-Exchange Resins with Solvents

The isotherms for the absorption of water by an ion-exchange resin depend on the type (types) of counterions, the content of the cross-linking agent, the hydrophilicity of the matrix and the cross-linking agent, and also on the characteristics of the steric structure of the resin matrix. According to Brunauer's classification [72], they can be assigned to the second type, characterised by multilayer adsorption without capillary condensation, With increase of the relative humidity of the vapour phase, the isotherms are nearly linear in the vicinity of zero [pressure ? (Ed. of Translation)]. For sulphonated polystyrene ion-exchange resins saturated with alkali metal or alkaline earth metal ions, the slopes of these curves are particularly high [68]. They are somewhat lower for sulphonated resins containing Ag^+ ions [68] and also organic ions. A sharp change in the isotherms in this region is characteristic of certain carboxylic acid resins in the H^+-form [4] and also for anion exchangers [76]. In the region of intermediate values of α the slope of the $\bar{n}_w - \alpha$ curve decreases compared with the first section but, as a rule, it is higher the higher is its value in the first section. The overall absorption of solvent along both sections of the isotherms is lower (sometimes much lower) than the maximum absorption of the solvent by the resin at $\alpha = 1$. Therefore the greatest change in swelling occurs in the region of relative humidity close to unity. The slopes of the isotherms in this region are also various. The following two series illustrate the variation of the swellability with the type of ion and α:[68]

$\alpha = 1$; $Mg^{2+} > H^+ > Li^+ > Na^+ > Ca^{2+} > NH_4^+ > K^+ > Ba^{2+} > Ag^+ \approx (CH_3)_4N^+$

$\alpha = 0{,}29$; $Mg^{2+} > H^+ > Ca^{2+} > Li^+ > Ba^{2+} > Na^+ > (CH_3)_4N^+ > NH_4^+ > K^+ > Ag^+$.

A change in the content of the cross-linking agent in the resin has the greatest effect along the third section of the isotherms: with increase in the degree of cross-linking, the swellability falls sharply. At lower values of α two opposed results have been noted: the swellability of resins with a high degree of cross-linking is lower for some resins [72,73] and higher for others [64,74,75] than for less cross-linked analogues (in this case the swelling isotherms at low and high values of α are reversed). Gregor [69] was the first to describe the reversal of the isotherms and explained it qualitatively. According to his hypothesis, in the region of low values of α in resins with a low content of cross-linking agents there is more intense interchain interaction, which reduces the degree of swelling. Because of its rigidity, the cross-linking agent limits this interaction, which leads to the reversal of isotherms. It is interesting to note that the isotherms for the absorption of solvents by non-cross-linked polyelectrolytes are also below the isotherms for the cross-linked analogues at low values of α and above them at high values. The reversal of isotherms is shown particularly clearly for macronetwork ion-exchange resins, which is evidently favoured by the interaction between the amide groups of the cross-linking agent and the monomer. It is noteworthy that,

in the hydration of macronetwork resins, data confirming Gregor's hypothesis were obtained: a change in the chain length of the cross-linking agent while retaining its relative content leads to the reversal of the isotherms[4]. The effect of the structural characteristics of resins on swellability may be followed in the usual sulphonated cation-exchange resins of the polymerisation type (macronetwork[75] and macroporous[76]) as examples. For the same content of cross-linking agent in KU-2 resin and in a macronetwork resin, their isotherms virtually merge in the first two regions of α values but differ significantly in the third, where there is a characteristic, particularly sharp rise for macronetwork resins, as a result of which the maximum swellabilities of the resins at $\alpha = 1$ differ severalfold. This phenomenon is associated with the large dimensions of the unit cell of the macronetwork resins and the smaller number of physical nodes in its structure. The isotherms for macroporous resins resemble those for macronetwork resins. They are also characterised by a sharp increase of swellability at α close to unity, but in this case the rise is not due to the formation of a homogeneous internal solution but is probably caused by capillary condensation in the pores of these resins. At lower values of α the hydration of macroporous resins takes place in the more condensed parts of the matrix†, i.e. as in the usual resins with a high content of cross-linking agent. The presence in the resin matrix of other types of hydrophilic centres influences all three sections of the isotherm for the absorption of solvent. Thus the presence of phenolic groups in KU-1 sulphonated cation exchanger appreciably enhances the equivalent content of the solvent in it compared with Dowex-50 × 2 resin (Na^+-form). On the other hand, the presence of amide groups in sulphonated cation exchangers has an insignificant effect on solvent absorption isotherms. The description of the factors influencing the shape of the isotherms for the absorption of solvent by resins shows that their quantitative representation by the function $\bar{n}_W = \varphi(\alpha)$ over the entire range of variation α is exceptionally difficult. Some authors proposed empirical equations describing the adsorption of water in narrow ranges of α. Recently the applicability of the BET equation to the adsorption of water in the region $0 < \alpha < (0.5\text{–}0.7)$ [77,78] has been extensively investigated. In this connection, it must be noted that the possibility of representing adsorption isotherms over a narrow range of α by the linear relation

$$\frac{\alpha}{v(1-\alpha)} = \varphi(\alpha)$$

is not sufficient proof that the adsorption mechanism is identical with that underlying the BET theory. It is necessary that the constants C and v_m (in the two-parameter equation) should lie within certain ranges consistent with the physical nature of the process. The second condition is that the measured temperature variation of the constant C should agree with the predictions of the theory. These problems were examined in greater detail by Flood[79].

The difference in the isotherms for the absorption of solvent by resins may be attributed to the different degrees of swelling of the resins in the three regions of the isotherms. The analysis of these effects is based mainly on the variation of the free energies of swelling with α (see p. 552).

†In Kunin's microspheres[56].

The difference in the isotherms for resins containing various amounts of the cross-linking agent may be formally based on osmotic theory in which it is assumed that the components in the resin phase are under a higher pressure ($p_0 + \pi$) than in solution (p_0).[64,68] This postulate, which constitutes the basis of the osmotic theory of ion exchange, has not been confirmed experimentally and must be regarded as hypothetical. One of its consequences is that the introduction of the cross-linking agent is equivalent to an increase of the pressure π. The pressure π is calculated from the isotherms for the absorption of water vapour by resins containing different amounts of the cross-linking agent. According to the osmotic theory, the chemical potential of the solvent in the resin may be represented thus:

$$\bar{\mu}_w = \bar{\mu}^0_w(T, p_0 + \pi) + RT \ln \bar{a}_w, \tag{21}$$

where $a_W \neq \varphi(\pi)$. Evidently

$$\frac{\partial \bar{\mu}^0_w(T, p_0+\pi)}{\partial \pi} = \frac{\partial^2 \Phi}{\partial \pi \partial n_s} = \bar{v}^0_w, \tag{22}$$

where $\bar{v}^0_W$ is the partial molar volume of the solvent in the standard state of the resin:

$$\bar{\mu}^0_w(T, p_0+\pi) = \bar{\mu}^0_w(T, p_0) + \int_{\pi=0}^{\pi} \bar{v}^0_w d\pi. \tag{23}$$

On expanding the partial molar volume of the solvent in series in terms of π, we obtain

$$\bar{\mu}^0_w(T, p_0+\pi) = \mu^0_w(T, p_0) + \int_{\pi}^{\pi} \left[\bar{v}^0_w(p_0) + \pi \frac{\partial \bar{v}_w(p_0)}{\partial \pi} + \right.$$
$$\left. + \frac{1}{2!}\pi^2 \frac{\partial^2 \bar{v}_w(p_0)}{\partial \pi^2} + \ldots\right] d\pi \simeq \bar{\mu}^0_w(T, p^0) + v^0_w\left(1 - \varkappa \frac{\pi}{2}\right)\pi = \bar{\mu}^0_w(T, p_0) + \pi \hat{w}^0_s, \tag{24}$$

where κ is the compressibility of water and v^0_W the partial molar volume of water in the standard state at a pressure $\pi/2$. Therefore the expression for the chemical potential of the solvent in the cross-linked resin assumes the following form:

$$\bar{\mu}_w(T, p_0+\pi) = \bar{\mu}^0_w(T, p_0) + \pi \hat{w}^0_w + RT \ln \bar{a}_w. \tag{25}$$

At equilibrium with the vapour of the solvent ($\bar{\mu}_W = \mu_W$)

$$\bar{\mu}^0_w(T, p_0) + \pi \hat{w}^0_w + RT \ln \bar{a}_s = \mu^0_w(T, p_0) + RT \ln \bar{\alpha}. \tag{26}$$

If the standard chemical potentials of the solvent in the resin and in the vapour are chosen the same ($\bar{\mu}^0_W = \mu^0_W$), then

$$\pi \hat{v}^0_w + RT \ln \bar{a}_w = RT \ln \bar{\alpha}. \tag{27}$$

Assuming that in a weakly cross-linked resin $\pi = 0$, we have

$$RT \ln \tilde{a}_w = RT \ln \tilde{\alpha}, \tag{28}$$

$\tilde{\alpha}$ being the relative vapour pressure of the solvent in equilibrium with the weakly cross-linked resin. We may note that an equation of type (22) can be applied not only to the standard chemical potential of the resin but also to the chemical potential of the resin with any solvent content (it is then necessary to satisfy also the condition of a constant moisture content in resins with different values of π):

$$\bar{\mu}_w(T, p_0+\pi) = \bar{\mu}_w(p_0) + \pi \hat{w}^0_w \text{ when } x_w = \text{const} \tag{29}$$

or, taking into account Eqns. (25) and (28) and putting $\bar{\mu}_W(p_0) = \tilde{\mu}_W(p_0)$:

$$\bar{\mu}^0_w(p_0) + \pi \hat{w}^0_w + RT \ln \bar{a}_w = \tilde{\mu}^0_w(p_0) + RT \ln \tilde{\alpha} + \pi \hat{v}^0_w$$
$$\text{when } \bar{x}_w = \tilde{x}_w. \tag{30}$$

For the above choice of standard states, we obtain‡

$$\bar{a}_w = \tilde{a}_w \text{ when } \bar{x}_w = \tilde{x}_w \quad (31)$$

or

$$\bar{f}_w = \tilde{f}_w \text{ when } \bar{x}_w = \tilde{x}_w . \quad (32)$$

Then it follows from Eqns. (27) and (28) that

$$\pi = \frac{RT}{\hat{v}_w^0} \ln \frac{\bar{\alpha}}{\tilde{\alpha}} \text{ when } \bar{x}_w = \tilde{x}_w . \quad (33)$$

Eqn. (33) is the starting point for the determination of the osmotic pressure. Since $\hat{v}_w^0$ corresponds to the partial molar volume of the pure solvent, it can be determined from tabulated data. Sometimes another expression is used for the pressure π:

$$\pi = \frac{RT}{v_w} \ln \frac{\bar{\alpha}}{\tilde{\alpha}} \text{ when } \bar{x}_w = \tilde{x}_w , \quad (34)$$

where v_w is the partial molar volume of the solvent in the swollen (cross-linked) resin.

Eqn. (34) is associated with another form of the expression for the chemical potential of the solvent in the resin, different from Eqn. (21):

$$\bar{\mu}_w(T, p_0 + \pi) = \bar{\mu}_w^0(T, p_0) + RT \ln \bar{x}_w \bar{\gamma}_w(p_0 + \pi) . \quad (35)$$

The possibility of this approach was first pointed out by Holm [81]. The principal difference between Eqns. (21) and (35) is due to the choice of different ideal reference systems§. In the first case it [the reference system? (Ed. of Translation)] is defined at the same pressure $p_0 + \pi$ as that of the components of the cross-linked resin and in the second case at a constant pressure p_0 (x_w is almost independent of π):

$$\frac{\partial \bar{\mu}_w(T, p_0 + \pi)}{\partial \pi} = RT \frac{\partial \ln \bar{\gamma}_w}{\partial \pi} = v_w , \quad (36)$$

where v_w is the partial molar volume of the solvent in the swollen cross-linked resin. It follows from Eqn. (36) that

$$RT \ln \bar{\gamma}_w(p_0 + \pi) = RT \ln \gamma_w(p_0) + \int_{\pi'}^{\pi} v_w d\pi \quad (37)$$

where $\bar{x}_w$ = const. In the region of not unduly low values [pressures (Ed. of Translation)], we have $\alpha \bar{v}_w$ = const. [82] and then

$$\bar{\gamma}_w(p_0 + \pi) = \bar{\gamma}_w(p_0) e^{\frac{\pi v_w}{RT}} \text{ when } \bar{x}_w = \text{const} . \quad (38)$$

At equilibrium between the cross-linked resin and the pure solvent

$$\bar{\mu}_w^0(p_0) + RT \ln \bar{a}_w(p_0 + \pi) = \mu_w^0(p_0) + RT \ln \bar{\alpha} \quad (39)$$

or

$$\bar{a}_w(p_0 + \pi) = \bar{\alpha} \quad (40)$$

when the standard chemical potentials are assumed to be equal in both phases. An analogous expression is obtained for the non-cross-linked resin:

$$\tilde{a}_w(p_0) = \tilde{\alpha} . \quad (41)$$

At equilibrium with vapour of the same composition

$$\frac{\bar{a}_w(p_0 + \pi)}{\tilde{a}_w(p_0)} = \frac{\bar{x}_w}{\tilde{x}_w} \cdot \frac{\bar{\gamma}_w(p_0 + \pi)}{\tilde{\gamma}_w(p_0)} = 1 . \quad (42)$$

‡Condition (31), based on osmotic theory, constitutes essentially the mathematical statement of the postulate indicated above.

§An ideal reference system is a system whose chemical potential satisfies the equation $\mu_i = \mu_i^0 + RT \ln x_i$.

Then using Eqn. (38) we obtain

$$\frac{\bar{x}_w}{\tilde{x}_w} \cdot \frac{\bar{\gamma}_w(p_0 + \pi, \bar{x}_w)}{\tilde{\gamma}_w(p_0, \tilde{x}_w)} = \frac{\bar{x}_w}{\tilde{x}_w} \cdot \frac{\tilde{\gamma}_w(p_0, \bar{x}_w)}{\tilde{\gamma}_w(p_0, \tilde{x}_w)} \cdot e^{-\frac{\pi v_w}{RT}} . \quad (43)$$

The moisture contents to which the activity coefficients correspond are indicated in Eqn. (43). We may note that in the derivation of Eqn. (43), as in Eqn. (30), the fundamental condition of the osmotic theory was employed, i.e.

$$\bar{\gamma}_w(p_0, \bar{x}_w) = \tilde{\gamma}_w(p_0, \bar{x}_w) .$$

Eqn. (43) can also be written as follows [see Eqns. (40) and (41)]:

$$\frac{\bar{a}_w(\bar{x}_w)}{\tilde{a}_w(\bar{x}_w)} = \frac{\bar{\alpha}(\bar{x}_w)}{\tilde{\alpha}(\bar{x}_w)} \cdot e^{-\frac{\pi v_w}{RT}} , \quad (44)$$

which is identical with Eqn. (34).

Comparison of Eqns. (33) and (34) shows that the osmotic pressure depends on the method of calculation, while the chemical potential does not. Compensation is achieved by means of different activity coefficients.

To determine the osmotic pressure in the resin phase, use is also made of the distribution of non-electrolytes between the solvent and the resin (the method of Ginzburg and Cohen). [83] Using Eqn. (25) for a solvent and a non-electrolyte, we obtain

$$\pi(v_w^0 - v_e^0) = RT \ln \frac{\bar{m}_e}{m_e} \frac{\bar{f}_e}{f_e} \cdot \frac{f_w}{\bar{f}_w} = RT \ln \left[K_e \frac{\bar{f}_e f_w}{f_e \bar{f}_w} \right] , \quad (45)$$

where K_e is the partition coefficient¶, $\bar{m}_e$ and m_e are the molalities of the non-electrolyte in the resin and in the external solution, and $\bar{f}_e$, f_e, $\bar{f}_w$, and f_w are the activity coefficients of the non-electrolyte and the solvent in the resin and in the solution respectively. It was found that, for a number of non-electrolytes (sucrose, glucose, arabinose, mannitol, raffinose, glycerol, and ethylene glycol), $\ln K_e$ is directly proportional to $v_w^0 - v_e^0$. The slope of the plot of $RT \ln K_e$ against $v_w^0 - v_e^0$ yields the osmotic pressure when the ratio $\bar{f}_e f_w / f_e \bar{f}_w$ varies insignificantly with $v_w^0 - v_e^0$. The osmotic pressures obtained in this way are fairly consistent with the values given by Eqn. (33), but they do exceed them by a factor of 2–3. This method must be regarded as an independent procedure for the determination of π, since it does not involve the postulates of the osmotic theory.

The qualitative description of the form of the solvent absorption isotherm shows that osmotic pressure increases with the content of the cross-linking agent in the range of relatively high values of α. The reversal of solvent absorption isotherms at low values of α is explained by the supporters of the osmotic theory as an effect of negative osmotic pressure, since it is believed that in this case π is zero in the reference ion-exchange resin (resins containing 0.5–2% of the cross-linking agent are usually chosen as a reference [62,64]).

The linear variation of the osmotic pressure with the equivalent volume of the resin V_e is also of interest [64]. Such relations have been found for Dowex-50 cation-exchange resins saturated with alkali metal ions and also for Dowex-1 anion-exchange resins saturated with halide ions [64]. In the exchange of tetraethylammonium and sodium ions on Dowex-50 × 8 Boyd and Schwarz [117] also observed a linear relation of the type

$$\pi = a \Delta V_e + b \quad (46)$$

¶The partition coefficient was found from the retention volumes of the non-electrolytes in a column experiment.

with the constants $a = 1.05$ cm^3 mole^{-1} atm^{-1} and $b = -239$ cm^3 mole^{-1}. It is nowadays believed[64] that relations of type (46) indicate that the resin may be regarded as a solid elastic body or as an elastomer. Putting Eqn. (46) in the form

$$\pi = k(V_e - V_e^0) = B\frac{\Delta V_e}{V_e^0}, \quad (47)$$

where V_e^0 is the value of V_e at $\alpha = 0$ and B is a constant which has the dimensions of the modulus of elasticity, it is possible to calculate from B an effective Young's modulus for resins. The values of Young's modulus for Dowex-50×8 and Dowex-1 × 6 resins are both 2.2×10^8 dyn cm^{-2}, which is higher by almost a power of ten than the values of Young's modulus for elastic polymers (in particular rubbers). We believe that another explanation of Eqn. (46) is also possible, not involving the characteristics of the elastic deformation of the polyelectrolyte network but associated with the characteristics of resin hydration in the region where $\alpha \to 1$ [at low moisture contents a and b in Eqn. (46) begin to vary with moisture content]. In this region of α values the slope of the solvent absorption isotherms and in particular the derivative $\partial n_w/\partial \ln \alpha$ varies relatively little with moisture content (a) and with the ionic form of the resin (b). Therefore, for each resin, it is possible to find a range of α values ($\alpha^* < \alpha < 1$) in which the following approximation is valid:

$$\Delta \bar{V}_e = \int_0^{\bar{n}_w} \bar{v}_w\, dn_w = \int_{-\infty}^{\ln \bar{\alpha}} \bar{v}_w \frac{\partial \bar{n}_w}{\partial \ln \bar{\alpha}} d\ln\alpha = \Delta v_e + \int_{\ln \bar{\alpha}^*}^{\ln \bar{\alpha}} \bar{v}_w \frac{\partial \bar{n}_w}{\partial \ln \bar{\alpha}} d\ln\alpha \simeq$$

$$\simeq \Delta v_e^0 + \overline{\bar{v}_w \frac{\partial \bar{n}_w}{\partial \ln \bar{\alpha}}} \cdot \ln \frac{\bar{\alpha}}{\bar{\alpha}^*} = \simeq v_e^0 + \beta \frac{v_w \pi}{RT} + \beta \ln \frac{\bar{\alpha}}{\bar{\alpha}^*} \simeq C + \gamma\pi, \quad (48)$$

where $\beta = v_w \frac{\partial \bar{n}_w}{\partial \ln \bar{\alpha}}$, γ, and C are constants, and Δv_e is the value of ΔV_e corresponding to the value of α at which the condition $\beta \simeq$ const. begins to hold.

If in the range of relative moisture contents considered $\partial \bar{n}_w/\partial \ln \bar{\alpha}$ and $\bar{v}_w$ are relatively constant, then Eqn. (48) is equivalent to Eqn. (47). The following comments may be made on these conditions: (a) the steepness of the isotherms for the absorption of solvents by resins saturated by univalent ions is the same for many resins in the vicinity of $\alpha = 1$;[68] the steepness of the solvent absorption isotherms changes on transition to polyvalent ions and also to organic ions[68,122,123]; thus it has been shown[73] that equations of type (46) for the Ba^{2+}- and H^+-forms of KU-2 resin have different constants a and b; (b) since the partial molar volume of the solvent in resins near $\alpha = 1$ changes relatively little with the moisture content of the resins[124], $\bar{v}_w \frac{\partial \bar{n}_w}{\partial \ln \bar{\alpha}}$ may indeed be regarded as constant in this region.

The significance of the concept of osmotic pressure in the resin is very important in the osmotic theory. According to one view this is a real pressure in the resin[64,85]. Subsequently it has been stated that the pressure π is merely a measure of all those changes in the system which are introduced by cross-linking[84]. Attempts have been made to associate π with capillary pressure[76]. In this case the strain in the polymeric skeleton of the sorbent is regarded as a response to capillary pressure, arising in consequence of the curvature of the outer surface of the resin grains.

In all cases the pressure π arises from the use of the relation between the chemical potential and the external pressure. The identity of the measure of the network effect with a real hydrostatic pressure is thereby asserted. So far there has been no experimental proof of the existence of an excess pressure in the resin compared with the solution. The method of Ginzburg and Cohen also does not provide a proof of the existence of the osmotic pressure, since the latter is used in the calculation. The application of the osmotic theory to isotherms for the absorption of solvents by resins with different degrees of cross-linking does not lead to an understanding of the essential feature of the swelling process. This is because a relation between the pressure π and the hydration mechanism has not been established. Somewhat greater advances have been made in the analysis of relations between the differential and integral free energies and α, the type of counterions, and the degree of cross-linking of the resins. When α (or $\bar{n}_w$) increases from zero, the integral free energies of swelling increase sharply but remain negative. The greatest changes occur in the absorption of the first solvent molecules, after which the free energies of swelling vary relatively little. However, it is precisely in this region that the resin absorbs the greatest amount of solvent. (This applies to an equal degree to integral and differential thermodynamic functions of swelling.) At high values of α, H_{sw} and S_{sw} for certain resins have a weak maximum, i.e. the changes in them with increasing α in the vicinity of $\alpha = 1$ are positive. The variation of the thermodynamic functions of swelling H_{sw} and S_{sw} with increase of α or $\bar{n}_w$ is explained at the present time mainly in the same way as the concentration dependence of the heats and entropies of hydration of crystalline salts[86].

The principal energy effects are the hydration of the fixed functional groups in the matrix and the counterions ($H_h < 0$ and $S_h < 0$) and also the dissociation of the fixed group–counterion pair ($H_d > 0$, $S_d > 0$). Since the overall values of H_{sw} and S_{sw} are negative, it is reasonable to suppose that the hydration effect exceeds the dissociation effect. The influence of the second effect prevails when α is close to unity in those cases where

$$\frac{\partial H_{sw}}{\partial \alpha} > 0 \text{ and } \frac{\partial S_{sw}}{\partial \alpha} > 0.$$

It should be borne in mind that in the swelling of resins the thermodynamic functions H_h, S_h, H_d, and S_d refer to interionic interactions only when the thermodynamic characteristics of the hydration and dissociation of the nonionogenic parts of the polymer (Φ_{hm}, H_{hm}, S_{hm}, Φ_{dm}, H_{dm}, S_{dm}) are treated independently. It was shown above that interchain interaction may be considerable even in somewhat swollen resins (the reversal of isopiestic lines). In dry resins this interaction is probably even more pronounced and can lead to an ordered arrangement of the polyelectrolyte chains. This is indicated in particular by electron microscope photographs of dehydrated resins obtained by Kargin et al.[87] and also the data of Laskorin et al.[17]

It is of great interest to establish a relation between the thermodynamic functions of swelling and the degree of order in the arrangement of chains in dry resins.

In the description of the dependence of Φ_{sw}, H_{sw}, and S_{sw} on α, it is usual also to indicate two further factors determined by the high molecular weight of the resin—the increase in the strain of the matrix on swelling and the mixing of the polymer chains with the solvent. The experimental methods for the determination of these effects are lacking; they can be estimated qualitatively with the aid of the theory of the swelling of cross-linked polyelectrolytes of Rice and Harris[88]. When the dehydrated cross-linked polyelectrolytes and the pure solvent are chosen as

the standard states, both contributions are negative. Calculations show that the contributions of these components (of the conformational entropy and enthalpy of swelling H_{SW} and S_{SW}) are indeed low [89]. For example, in the swelling of Dowex-50 cation-exchange resin in the K^+-form (from the dry resin to the resin with the maximum degree of swelling) the conformational free energy is −0.43 and −0.81 kcal equiv.$^{-1}$ for divinylbenzene contents of 3 and 15% respectively, which amounts to 10 and 20% of the integral free energy of swelling. Thus the integral free energy of swelling Φ_{SW} is affected by at least five factors.

$$\Phi_{sw} = \Phi_h + \Phi_d + \Phi_{con} + \Phi_{hm} + \Phi_{dm} \qquad (49)$$

However, at present it is possible to determine experimentally only Φ_{SW}, so that the contributions of each separate effect remain unknown†. This is one of the main obstacles to the development of a theory of swelling of cross-linked polyelectrolytes, since it makes it impossible to obtain quantities necessary to simulate the individual effects and to test them. Further accumulation of experimental data in this field is necessary.

Ion-exchange resins have come to be regarded as electrolytes with a high concentration of ions set up by their fixation on the matrix. It is interesting to note some similarity and also a difference in the thermodynamic functions of the hydration of resins and crystalline salts (using heat as an example): 1. H_{SW} changes sharply on sorption of the first solvent molecules and then the variation is slight. The heat of solution in water of a crystalline salt varies relatively little with dilution in the region close to the saturated solution. On the other hand the heats of solution of salts in organic solvents are much more exothermic and their variation with concentration is also more pronounced. Possibly the effect of the organic resin matrix is identical with the effect of the organic solvent. 2. The relation between the enthalpies and entropies of hydration of salts is close to linearity [90]. Fig. 3 shows that there is also a linear relation between H_{SW} and S_{SW} for resins in water. Points corresponding to a given degree of cross-linking of the resins in different ionic forms and also points corresponding to resins with different contents of the cross-linking agent but in the same ionic form are plotted on this curve. We may note that the thermodynamic functions of the swelling of Dowex-50 resins depends little on the degree of cross-linking while those for macronetwork resins depend on cross-linking to a much greater extent. With increase in the degree of cross-linking of macronetwork resins and Dowex-50 resins, the absolute values of H_{SW} and S_{SW} increase. The thermodynamic functions H_{SW} and S_{SW} for non-cross-linked polymethylstyrenesulphonic acid and its sodium salt exceed the corresponding thermodynamic functions for cross-linked resins (up to 15% of divinylbenzene). Nevertheless these values are consistent with the relations presented in Fig. 3. The existence of relations of a similar form between the enthalpies and entropies of swelling of resins and of the hydration of crystalline salts shows that there is a profound analogy between these processes. As far as we are aware, these relations have not been explained.

†Analogous problems occur in the theory of electrolyte solutions at moderate and high concentrations where the concentration variation of the heats and entropies of hydration is also determined by a number of separate factors [86].

The mechanism of the absorption of water vapour by ion-exchange sorbents has also been investigated by analysing the differential free energies, enthalpies, and entropies of swelling. The differential thermodynamic functions of swelling have been used most successfully for the analysis of the mechanism of the interaction with the solvent, particularly in the region of low values of α.

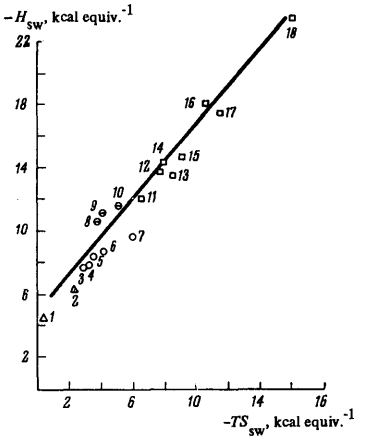

Figure 3. Relation between the enthalpies and entropies of swelling of resins in water: 1) Dowex-50 × 3, K^+; 2) Dowex-50 × 15, K^+; 3) Dowex-50 × 1, Na^+; 4) Dowex-50 × 3, Na^+; 5) Dowex-50 × 8, Na^+; 6) Dowex-50 × 15, Na^+; 7) KU-2, Na^+; 8) Dowex-50 × 0.5, H^+; 9) Dowex-50 × 3, H^+; 10) Dowex-50 × 8, H^+; 12) KU-2, H^+. Macronetwork resins with different amounts of cross-linking agent: 11) decamethylenedimethacrylamide (DMDMA), 16%, H^+; 13) DMDMA, 16%, Na^+; 14) hexamethylenedimethacrylamide (HMDMA), 9%, Na^+; 15) ethylenedimethacrylamide (EDMA), 16%, H^+; 16) HMDMA, 16%, Na^+; 17) EDMA, 16%, Na^+; 18) HMDMA, 41%, Na^+.

The work of Gluekauf and Kitt [91] largely initiated these investigations. The hydration of ion-exchange resins is regarded as a stepwise adsorption process. Analysis of the thermodynamic functions of the sorption of water shows that the first water molecule is sorbed exclusively by an SO_3^- group fixed on the matrix. Such a mechanism of the absorption of water has been attributed to all the salt-forms of sulphonated resins. The scatter of the differential thermodynamic functions of different salt-forms is probably due to different interactions between the non-hydrated cations and the hydrated groups. It has also been shown that the second and subsequent hydration shells are formed as a result of the hydration of the cation.

The enthalpy and entropy components for the sorption of the first, second, and subsequent solvent molecules per functional group of the resin have been calculated from the temperature variation of the water vapour absorption isotherms. Analysis of the heats and entropies of solvent absorption led to the following conclusions. If there is one molecule per active group, then its interaction with the counterion and also the interaction of the counterion with the water molecule is not a linear function of the ionic radius alone, i.e. is not purely Coulombic. For large ions

such as Ag^+ and Cs^+, these interactions may depend in addition on factors such as polarisation. The addition of a second water molecule probably loosens somewhat the structure of the sorption complex and weakens the polarisation interactions occurring over short distances. Beyond this point Coulombic interaction becomes typical for the entire series of alkali metal ions. Later these methods were criticised both from the standpoint of the validity of the thermodynamic description of the hydration of resins and from the standpoint of the reliability of the experimental data[89,92]. The inflections in the plots of the thermodynamic functions obtained from the temperature variation of the isotherms were not confirmed by calorimetric measurements on similar resins[89,92-94]. We may note that for all the ionic forms investigated by Gluekauf and Kitt[91] the error in the determination of the differential thermodynamic functions is approximately the same and yet the curves for different ionic forms differ significantly. The H^+-, Ba^+-, and Ca^{2+}-forms of the resins do not show inflections, while for the Li^+-, Ag^+-, Na^+-, K^+-, NH_4^+-, and Cs^+-forms the inflections in the thermodynamic functions are fairly pronounced. Recently the inflections in the differential thermodynamic functions for certain types of sorbents have been observed also by calorimetric methods[95,97]. Nevertheless, final conclusions concerning the presence or absence of inflections in the differential thermodynamic functions of swelling would be premature, since in all the studies of which we are aware no estimate was made of the reliability of these functions when inflections are present.

The mechanism of the hydration of ion exchangers has been vigorously investigated also by a wide variety of physical methods. The study of the infrared spectra of thin films (up to 5 μm) of sulphonated polystyrene led to the conclusion[29,30] that the hydration of the salt-forms of sulphonated resins begins with the interaction of water with the counterion. On combining with a first water molecule, the cation becomes somewhat removed from the fixed group in the sorbent. The subsequent hydration shells are formed both between the counterion and the fixed group and in the space surrounding both ions. These findings are based mainly on the study of the stretching and deformation vibrations of sorbed water molecules. However, direct investigation of the frequencies of interionic vibrations[96] in films of polyvinylsulphonic [polyethylenesulphonic ? (Ed. of Translation)] acid and its salts shows that, on absorption of the first solvent molecule, the distance between ions changes relatively little. The interionic distance increases but this change is insufficient for the incorporation of water molecules between the ions. It was also shown that the water of hydration does not participate in ionic vibrations, i.e. there is no rigid binding of water molecules. On this basis, it was concluded that ion pairs and not individual ions are hydrated in ion-exchange films. Thus there exist different explanations of the mechanism of primary hydration. The reason for this remains obscure. With decrease in crystallographic ionic radius (from Rb^+ to Li^+ and from Ba^{2+} to Mg^{2+}), the interaction of ions with water molecules intensifies. The splitting of asymmetric stretching vibrations of the SO_3^- group and in particular the independence of this splitting of moisture content for all counterions shows that in all cases the counterion is located asymmetrically in the pyramidal structure of the sulphonato-group, namely in the vicinity of one of the oxygen atoms. The following counterions have been examined[29,30]: H^+, Li^+, Na^+, K^+, Rb^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, NH_4^+, $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$. In the hydration of the hydrogen-forms of sulphonated resin films aggregates of several hydrogen-bonded water molecules having the general formula $H_{4n+3}O_{2n+1}$ (n is independent of the relative moisture content) are formed. For all moisture contents, hydronium ions are also distributed asymmetrically in relation to the sulphonato-group, the proton being capable of migrating readily from one water molecule in the aggregate to another. Judging from the differential thermodynamic functions, the mechanism of the primary hydration of carboxylic acid cation exchangers[98] in the H^+-form is similar to the mechanism of the hydration of the salt-forms of sulphonated resins discussed above[96]. After the formation of the primary hydration shell, polymolecular condensation of water takes place. On the other hand, the mechanism of the hydration of the salt-forms of carboxylic acid cation exchangers is probably similar to the mechanism of the hydration of the salt-forms of sulphonated cation-exchange resins proposed by Gluekauf and Kitt[91].

The NMR method has been used to characterise moisture absorption by hydrogen-forms of Dowex-50 resin with different degrees of cross-linking[33,35-39]. Quantitative information about the state of water in resins has been obtained from chemical shifts and changes in signal width. A decrease in the moisture content of resins leads to an increase of signal width and its maximum is displaced towards lower field strengths. This shift is different for resins with different amounts of the cross-linking agent. The chemical shift depends also on the presence of hydrogen bonds in the sorbed water. Therefore at a low moisture content, when the normal structure of water breaks down due to the vigorous interaction of water molecules with the polar groups of the solvent, the resonance band is displaced towards lower field strengths as in ordinary water on increase of temperature. The chemical shift towards higher magnetic field strengths is proportional to the number of benzene rings and to the increase of the distance between the sulphonato-group and the molecules of water of hydration. The width of the resonance absorption band for sorbed water is much higher than for pure water (20–100 Hz compared with 0.5 Hz) but is less than for ice. This means that water molecules in the resin phase are in a state of rapid albeit restricted motion. The increase in absorption band width has been attributed to the inhomogeneity of the magnetic field of the resin grains. At low moisture contents not all the active groups of the resin can be hydrated to an equal extent and therefore different chemical shifts are possible. Then the observed resonance band will consist of bands corresponding to several different states of the water molecules, which is the reason for its broadening. Together with the absorption band due to sorbed water, an absorption band due to the water between the grains is also observed. The disappearance of this second band on reducing the moisture content of resins and the reversible sharpening and smoothing out of the bands on lowering and raising the temperature respectively show that there is exchange between the protons of the water in the resin and outside. The kinetics of this exchange have been investigated using heavy water and the results have been interpreted by the method of Boyd and Soldano[99]. The diffusion coefficient proved to be of the order of 800×10^{-6} cm^2 s^{-1}. The NMR method enables the heterogeneity of resins to be quantitatively characterised. The presence of a single narrow absorption band due to internal water indicates a high degree of homogeneity of the materials employed. This homogeneity must be regarded as indicating a constant time-average environment of the molecules of sorbed water. Since one cannot exclude the possibility of the presence in resin

grains of density gradients of the cross-linking agent or concentration gradients of the active groups, this result may be evidence of rapid exchange between water molecules in different states. The exchange within grains is considered, since it has been shown by the same method that the exchange of water molecules between grains is much slower.

Thus the narrow resonance absorption line may be due to kinetic causes (migration of water molecules and structural features of the resins such as a constant density of the cross-linking agent and of the concentration of active groups throughout the bulk of the grain. By studying the temperature variation of the half-width of the resonance band, it is possible to distinguish both components in individual cases, since the first of these depends on the change in temperature and the second does not.

III. FREE ENERGY OF ION EXCHANGE

There have been many studies where the ion-exchange equilibria between inorganic and also between organic and inorganic ions were investigated [100–105]. The nature of the ion has a significant effect on the selectivity of its absorption: factors which are dominant in the first case may be secondary in the second. These studies, in particular by Boyd and coworkers [101,102], confirm the qualitative hypotheses concerning the principal effects which determine the thermodynamic selectivity (electrostatic interaction, different structure of the hydration shells of ions in the resin compared with the solution, effect of solvent structure on the interaction between ions, effect of resin matrix, etc.). Among these qualitative concepts, mention should be made of the theories of Daimond [107], Eisenman [108], and Izmailov [109]. Further development of these concepts requires, however, a knowledge of the thermodynamic functions associated with the different states of the solvent in the resin and in solution. In this connection it is necessary to consider the methods of calculation of the thermodynamic functions associated with the changes in the hydration of resins during ion exchange.

Experimental data show that in ion exchange the state of equilibrium depends on the change in the degree of swelling and hence on the factors which determine the interaction between the resin and the solvent. When the selective absorption of ions is determined by the reduction of the enthalpy of the system, i.e. when the electrostatic interaction with the fixed group increases, their interaction with the solvent is weakened. When Li^+ ions are displaced by other alkali metal ions from Dowex-50 resin, the selectivity increases on going from Na^+ to Cs^+ ($\Delta H^0 < 0$) and the swellability of the resin decreases steadily. Since the affinity of the carboxy-group for the proton is particularly high, the swellability of carboxylic acid cation exchangers in the H^+-form is much lower than that of the salt-forms. The selective sorption of quaternary ammonium ions and a number of other organic cations on Dowex-50 resins is also accompanied by a decrease of the swelling of the resin [62]. In those cases where the decrease of the free energy of ion exchange is due to an entropy increase, the swellability of the resin may decrease to a smaller extent, while in some others it can increase [110]. In the early theory of ion exchange (Gregor [80], Gluekauf [111]) it was assumed that the change in the degree of swelling of the resin in ion exchange determines entirely its specificity. The effect of swelling on selectivity in this theory is taken into account quantitatively in two ways: in terms of the osmotic work $\pi\Delta v_i$ (π is the swelling pressure and Δv_i the difference between the partial molar volumes of the resinates) and also to some extent in terms of the activity coefficients of the resinates. In the two methods of choosing a reference system in the osmotic theory (see Section II), there is a possibility of two formally different expressions for the thermodynamic ion-exchange equilibrium constant‡. If the reference states in the solution§ and in the resin are chosen at different pressures (in solution $p = 1$ atm and in the resin $p = \pi$), the following expression is obtained [81] for K_B^A:

$$RT \ln K_B^A = \int_{p_0}^{p_0} [z_B v_A^0 (p, m_A, m_B) - z_A v_B^0 (p, m_A, m_B)]\, dp, \qquad (50)$$

where

$$K_B^A = \frac{\bar{a}^{z_A}_B}{\bar{a}^{z_B}_A} \frac{a^{z_B}_A}{a^{z_A}_B} = \tilde{K}_B^A \frac{\bar{\gamma}^{z_A}_B}{\bar{\gamma}^{z_B}_A} = \tilde{K}_B^A \frac{\bar{\gamma}^{z_A}_B}{\bar{\gamma}^{z_B}_A} \cdot \frac{\gamma^{z_B}_A}{\gamma^{z_A}_B},$$

$$RT \ln \tilde{K}_B^A = RT \ln \frac{\gamma^{z_A}_B}{\gamma^{z_B}_A} - RT \ln \frac{\bar{\gamma}^{z_A}_B}{\bar{\gamma}^{z_B}_A} (\pi, m_A, m_B) + \int_{p_0}^{p_0+\pi} (z_B v_A^0 - z_A v_B^0)\, dp \simeq$$

$$\simeq RT \ln \frac{\gamma^{z_A}_B}{\gamma^{z_B}_A} - RT \ln \frac{\bar{\gamma}^{z_A}_B}{\bar{\gamma}^{z_B}_A} (\pi, m_A, m_B) + \pi [z_B v_A^0 - z_A v_B^0]. \qquad (51)$$

Here v_B^0 and v_A^0 are the partial molar volumes of the resinates in the standard state. In this equation the swellability of the resin influences two terms—the last and the penultimate. The term $RT \ln (\bar{\gamma}^{z_A}_B / \bar{\gamma}^{z_B}_A)$ takes into account also the interaction of the ions with the resin and with one another. On the other hand, when all the reference states are chosen at the same pressure, for example, atmospheric, then the following expression is obtained for K_B^A (the standard states of all the components are the same¶):

$$\ln K_B^A = 0,$$

$$RT \ln \tilde{K}_B^A = RT \ln \frac{\gamma^{z_A}_B}{\gamma^{z_B}_A} - RT \ln \frac{\bar{\gamma}^{z_A}_B}{\bar{\gamma}^{z_B}_A} (p_0, m_A, m_B) + \int_{p_0}^{p_0+\pi} (z_B v_A - z_A v_B)\, dp \simeq$$

$$\simeq RT \ln \frac{\gamma^{z_A}_B}{\gamma^{z_B}_A} - RT \ln \frac{\bar{\gamma}^{z_A}_B}{\bar{\gamma}^{z_B}_A} (p_0, m_A, m_B) + \pi [z_B v_A - z_A v_B]. \qquad (52)$$

In Eqn. (52) the activity coefficients in the resin phase are independent of pressure and consequently of the swelling of the given cross-linked resin. The effect of swellability on selectivity is associated with the last term on the right-hand side. However, this term also takes partially into account the deviation of the system from ideality. Thus in none of the cases is it possible to distinguish the component which depends entirely on the change in swellability during ion exchange†. The quantities v_B^0 and v_A^0 in Eqn. (51) correspond to the partial molar volumes of the hydrated resinates at infinite dilution and can be estimated approximately from the corresponding values for the low-molecular electrolytes which are suitable models for

‡Holm [81] showed that both equations can be obtained from a more general equation with a different choice of reference states.

§The reference state in solution corresponds to infinite dilution.

¶For a more general case, see Holm [81].

†As pointed out correctly by Holm [81], for the same reason the osmotic free energy and the energy of interionic interaction introduced by Boyd [82] are not independent.

resins. In order to find the osmotic work from Eqns. (51) and (52), it is necessary to employ isopiestic measurements (which determine πv_W) and also pyknometric measurements (which determine v_W and Δv_i). When Eqn. (52) is used, it is possible to indicate a simpler method for the determination of osmotic work, involving isopiestic data only. For many resins, there is a relation (in some cases linear) between the swelling pressure π and the equivalent resin volume V_e:[64]

$$\pi = F(V_e) \quad . \tag{53}$$

According to the definition of the equivalent volume,

$$z_A z_B dV_e = (z_B v_A - z_A v_B)\, d\theta_A + z_A z_B v_W dn_W , \tag{54}$$

where v_A, v_B, and v_W are the partial molar volumes of the resinates A and B and the solvent and θ_A is the equivalent fraction of the ions A in the sorbed state. Hence it can be shown [112] that

$$\pi(z_B v_A - z_A v_B) = z_A z_B \int_0^{\bar{n}_W} \frac{\partial w_W}{\partial \theta_A} dn_W \quad . \tag{55}$$

The integral on the right-hand side of the equation can be calculated provided that the absorption isotherms for the vapour of the given and reference resin are known for several ionic compositions.

In the osmotic theory there are several methods for the calculation of the activity coefficients of the resinates (and also their ratios) from the solvent absorption isotherms. A large group of studies (Gluekauf, Gregor, Soldano, and others) deals with the determination of the dependence of the osmotic coefficient of the solvent in the resin on the molality of the counterions, the calculation by the Gibbs–Duhem equation of the activity coefficients of the mono-ionic forms, and their combination of determine the activity coefficients of ions in resins having a mixed composition [100,111,113,115]. Soldano showed [114] that the Harned rule does not apply to the resin phase and an empirical relation with the molality in the resin has been proposed for the interaction coefficients, on the basis of which it proved possible to obtain satisfactory agreement between the calculated and experimental $\tilde{\tilde{K}}_B^A$ in the exchange of a series of univalent and divalent ions. Boyd's method [82] is more rigorous from the thermodynamic standpoint. For subsequent discussion, it is convenient to consider the derivation of Boyd's equation by a method somewhat different from that employed in the original paper [112].

If the resin is regarded as a three-component system (two counterions and the solvent), the McKay relation becomes

$$\left.\frac{\partial \ln \bar{a}_B}{\partial \bar{n}_W}\right|_{\bar{n}_A \bar{n}_B} = \left.\frac{\partial \ln \bar{a}_W}{\partial \bar{n}_B}\right|_{\bar{n}_A \bar{n}_W} , \tag{56}$$

$$\left.\frac{\partial \ln \bar{a}_A}{\partial \bar{n}_W}\right|_{\bar{n}_A \bar{n}_B} = \left.\frac{\partial \ln \bar{a}_W}{\partial \bar{n}_A}\right|_{\bar{n}_B \bar{n}_W} . \tag{57}$$

Eqns. (56) and (57) are now multiplied by z_A and z_B respectively. On subtracting Eqn. (57) from Eqn. (56) and remembering‡ that

$$\frac{\bar{a}_B}{\bar{a}_A} = \frac{\bar{m}_B \bar{\gamma}_B}{\bar{m}_A \bar{\gamma}_A} = \frac{\bar{x}_B \bar{\gamma}_B}{\bar{x}_A \bar{\gamma}_A} , \tag{58}$$

where $\bar{m}_B$ and $\bar{m}_A$ are the molalities of the counterions, $\bar{\gamma}_B$ and $\bar{\gamma}_A$ the molal activity coefficients, and $\bar{x}_B$ and $\bar{x}_A$ the equivalent fractions, we obtain the following equation:

$$\left.\frac{\partial \ln \dfrac{\bar{\gamma}_B^{z_A}}{\bar{\gamma}_A^{z_B}}}{\partial \bar{n}_W}\right|_{\bar{n}_A, \bar{n}_B} = z_A \left(\frac{\partial \ln \bar{a}_W}{\partial n_B}\right)_{\bar{n}_A, \bar{n}_W} - z_B \left(\frac{\partial \ln \bar{a}_W}{\partial \bar{n}_A}\right)_{\bar{n}_B, \bar{n}_W} . \tag{59}$$

We shall now convert the independent variables $\bar{n}_B$, $\bar{n}_A$, $\bar{n}_W$ to the variables $\bar{\theta}_B$, $\bar{\theta}_W$, and n, where

$$\bar{\theta}_B = \frac{\bar{n}_B z_B}{\bar{n}_A z_A + \bar{n}_B z_B} = \frac{\bar{n}_B z_B}{n} = \text{equivalent fraction of the ion B in the resin} \tag{60}$$

and

$$\bar{\theta}_W = \frac{\bar{n}_W}{\bar{n}_A z_A + \bar{n}_B z_B} = \frac{\bar{n}_W}{n} = \text{equivalent content of the solvent} \quad (\bar{n} = \bar{n}_A z_A + \bar{n}_B z_B). \tag{61}$$

It can be shown [125] that

$$z_A \left(\frac{\partial \ln \bar{a}_W}{\partial \bar{n}_B}\right)_{\bar{n}_A, \bar{n}_W} - z_B \left(\frac{\partial \ln \bar{a}_W}{\partial \bar{n}_A}\right)_{\bar{n}_B \bar{n}_W} = \frac{z_A z_B}{n} \left(\frac{\partial \ln \bar{a}_W}{\partial \theta_B}\right)_{\bar{\theta}_W, \bar{n}} . \tag{62}$$

Then we obtain from Eqn. (59), taking into account Eqn. (62),

$$\left.\frac{\partial \ln (\bar{\gamma}_B^{z_A}/\bar{\gamma}_A^{z_B})}{\partial \theta_W}\right|_{\theta_B n} = z_A z_B \left(\frac{\partial \ln \bar{a}_W}{\partial \theta_B}\right)_{\theta_B n} . \tag{63}$$

We shall now consider Eqn. (63) under the condition n = const., i.e. when the exchange capacity is constant [taking into account Eqn. (40)]:

$$\ln \frac{\bar{\gamma}_B^{z_A}}{\bar{\gamma}_A^{z_B}} = \ln \frac{\bar{\gamma}_B^{z_A}}{\bar{\gamma}_A^{z_B}} (\text{отсч}) + z_A z_B \int_{\theta_{W(\text{ref.})}}^{\bar{\theta}_W} \frac{\partial \ln a}{\partial \theta_B} d\theta_W , \tag{64}$$

where $\theta_{W(\text{ref})}$ is the equivalent content of the solvent in the reference state of the resin (for example in the resin swollen to the maximum extent). The integral on the right-hand side of Eqn. (64) is equal to the integral J_R in Boyd's paper [82]§ to within a numerical multiplier:

$$\int_{\theta_{w(\text{ref.})}}^{\bar{\theta}_n} \frac{\partial \ln \bar{a}_W}{\partial \bar{\theta}_B} d\theta_W = \frac{\partial}{\partial \bar{\theta}_B} \left[\int_{\bar{\theta}_{w(\text{ref.})}}^{\bar{\theta}_W} \ln \bar{a}_W d\theta_W\right]_{\bar{\theta}_W, \bar{\theta}_{w(\text{ref.})}} = -\int_0^{\ln \bar{a}_W} \frac{\partial \bar{\theta}_W}{\partial \bar{\theta}_B} d \ln a_W =$$

$$= 55.51 \int_0^{\ln \bar{a}_W} \frac{\partial \frac{1}{m}}{\partial \bar{\theta}_A} d \ln a_W = 55.51\, J_R . \tag{65}$$

The integral J_R [or the integral in Eqn. (64)] is calculated from isopiestic data for several ionic compositions of the resin. In Eqn. (52) the apparent ion-exchange equilibrium constant $\tilde{\tilde{K}}_B^A$ at $\pi = 0$ depends on the ratio of the activity coefficients of the cross-linked resin $[\ln (\bar{\gamma}_B^{z_A}/\bar{\gamma}_A^{z_B})(p_0 m_A m_B)]$. If it is assumed, as in the osmotic theory, that they can be equated to the activity coefficient of the non-cross-linked resin having the same ionic composition, i.e:

$$\ln \frac{\bar{\gamma}_B^{z_A}}{\bar{\gamma}_A^{z_B}}(p_0, m_A, m_B) = \ln \frac{\bar{\gamma}_B^{z_A}}{\bar{\gamma}_A^{z_B}}(p_0, m_A, m_B) , \tag{66}$$

then substitution of Eqns. (64) and (66) in Eqn. (52) yields

‡In Boyd's theory the molal concentration scale is employed.

§In Boyd's paper [82] there is a misprint: the sign on the right-hand side of Eqn. (7e) and of the integrals in the subsequent equations should be reversed. This misprint was eliminated from Boyd's subsequent papers [116,117]. Nevertheless it has found its way into certain monographs on ion exchange (see, for example, Helfferich [100]).

the required relation between $\tilde{\tilde{K}}_B^A$ and a function of the swellability of the cross-linked resin:

$$RT\ln\tilde{\tilde{K}}_B^A = RT\ln\frac{\bar{\gamma}_B^{z_A}}{\bar{\gamma}_A^{z_B}} - RT\ln\frac{\tilde{\gamma}_B^{z_A}}{\tilde{\gamma}_A^{z_B}}\text{ (ref.)} + z_A z_B\int_{\bar{\theta}_{w(ref.)}}^{\bar{\theta}_w}\left(\frac{\partial\ln\tilde{a}_w}{\partial\tilde{\theta}_B}\right)_{\theta_w,\pi}d\theta_w + \pi[z_B v_A - z_A v_B]. \quad (67)$$

The effect of the swellability of the cross-linked resin is shown in the quantities π, $\bar{\theta}_w$, v_A, and v_B. The term $RT\ln(\bar{\gamma}_B^{z_A}/\bar{\gamma}_A^{z_B})$ (ref.) is determined by applying Eqn. (67) to a weakly cross-linked resin, from the absorption isotherm of which the integral $J_R(\bar{\theta}_w = \bar{\theta}_{w(ref)},\ \pi = 0)$ is calculated:

$$RT\ln\tilde{\tilde{K}}_B^A\text{ (ref.)} = RT\ln\frac{\bar{\gamma}_B^{z_A}}{\bar{\gamma}_A^{z_B}} - RT\ln\frac{\tilde{\gamma}_B^{z_A}}{\tilde{\gamma}_A^{z_B}}. \quad (68)$$

The ratio of the activity coefficient in the external solution is the same in Eqns. (67) and (68) if the apparent ion-exchange equilibrium constants $\tilde{\tilde{K}}_B^A$ and $\tilde{\tilde{K}}_B^A$ (ref.) are determined for the case where the cross-linked and the weakly cross-linked reference resins are in contact with the same solutions. Substitution of Eqn. (68) in Eqn. (67) gives

$$RT\ln\tilde{\tilde{K}}_B^A = RT\ln\tilde{\tilde{K}}_B^A\text{ (ref.)}) + \int_{\bar{\theta}_{w(ref.)}}^{\bar{\theta}_w}\left(\frac{\partial\ln\bar{a}_w}{\partial\theta_B}\right)_{\theta_w,\pi}d\theta_w + \pi[z_B v_A - z_A v_B]. \quad (69)$$

Eqn. (69) permits the calculation from a combination of isopiestic and pyknometric data [and for systems obeying Eqn. (53) isopiestic data alone] of the ratio of the apparent ion-exchange equilibrium constants for the cross-linked and reference resins: $\tilde{\tilde{K}}_B^A/\tilde{\tilde{K}}_B^A$ (ref.). To determine $\tilde{\tilde{K}}_B^A$ for the cross-linked resin, it is also necessary to determine experimentally $\tilde{\tilde{K}}_B^A$ (ref.). It is important to note that, when $\tilde{\tilde{K}}_B^A$ (ref.) and the integral J_R are known for any one reference resin, it is possible to calculate $\tilde{\tilde{K}}_B^A$ for any resin which obeys condition (66). When Eqn. (51) is used, it is also possible to arrive at Eqn. (69) with the aid of the following relation between the activity coefficients of the components and pressure:

$$RT\frac{\partial\ln\bar{\gamma}_i(\pi)}{\partial p} = v_i - v_i^0\frac{\partial p_r}{\partial p}, \quad (70)$$

where p_r is the pressure in the system in the reference state. In Eqn. (51) it is assumed that the reference states are chosen at the same pressures as those present in the real system. In ion-exchange resins such a pressure is the osmotic pressure. Combination of the integrals in Eqn. (70) for counterions A and B leads to the following relation:

$$RT\ln\bar{\gamma}_B^{z_A}/\bar{\gamma}_A^{z_B}(\pi, m_A, m_B) = RT\ln\bar{\gamma}_B^{z_A}/\bar{\gamma}_A^{z_B}(p_0, m_A, m_B) + \int_{p_0}^{p_0+\pi}(z_A v_B - z_B v_A)\,dp - \pi(z_A v_B^0 - z_B v_A^0). \quad (71)$$

When Eqn. (71) is substituted in Eqn. (51), Eqn. (69) is obtained. Therefore the methods for the determination of $\pi\Delta v_i$ and $RT\ln[(\bar{\gamma}_B^{z_A}/\bar{\gamma}_A^{z_B})(p_0, m_A, m_B)]$ described above have a direct bearing on the analysis of the selectivity of ion exchange from the standpoint of this version of the osmotic theory. Boyd suggested that condition (66) applies to ion-exchange resins of a single type, for example sulphonated polystyrene resins cross-linked with divinylbenzene¶. Comparison of the values of $\tilde{\tilde{K}}_B^A$ calculated by Eqn. (69) and found experimentally shows that the methods of the osmotic theory give a satisfactory quantitative representation of the variation of the apparent ion-exchange equilibrium constant with the degree of cross-linking of the resin (or its swellability). At present such comparisons have been made both for low values of $\pi\Delta v_i$ together with high contributions of the activity coefficients (exchange of alkali metal ions on Dowex-50 cation exchangers [82], exchange of halide anions on anion exchangers [116]) and for high values of $\pi\Delta v_i$ together with relatively smaller contributions of the activity coefficients (tetramethylammonium–sodium exchange on sulphonated polystyrene resins). It is interesting that in the latter case the theory predicts the reversal of selectivity, which is observed experimentally. In all cases the discrepancy between the theory and experiment increases with the degree of cross-linking of the resin. No attempt has been made to treat this discrepancy quantitatively.

Together with the osmotic theory, other methods have been developed, among which particularly interesting are the formally thermodynamic methods unrelated to any models or assumptions apart from those which follow from the nature of thermodynamic laws. Such are the methods of Bonner and Davidson [118,119] and Gaines and Thomas [120,121]. Despite the fact that the first method does not take the solvent into account while the second does involve an estimate of its contribution, both methods yield virtually identical activity coefficients and ion-exchange equilibrium constants. If can be readily shown that the reason for this lies in the nature of the standard states of the resins (pure monofunctional forms in equilibrium with an infinitely dilute solution or pure solvent). When other standard states are employed, the thermodynamic contribution of the solvent increases. Although the choice of standard chemical potentials is in principal arbitrary, it is nevertheless useful to choose them so that the contribution of each component involved in the method is convenient for experimental estimation. Only then is it possible to compare the changes of the individual effects when the type of ion, the type of resin, etc. are varied, i.e. it is possible to obtain a quantitative relation with models. We believe that the choice of dehydrated monofunctional forms of ion-exchange resins as the standard states satisfies these requirements. We shall examine the calculation of the activity coefficient and ion-exchange equilibrium constant for this choice of standard states. To do this, Eqn. (63) is applied to a cross-linked resin remembering that in this case the activity of the solvent in the resin is assumed equal to its activity in the vapour phase regardless of the content of the cross-linking agent. Integration of Eqn. (63) from the state of the dehydrated resin ($\bar{\theta}_w = 0$) to the state of the resin swollen to the maximum extent in the solvent gives

$$\ln\frac{\bar{\gamma}_B^{z_A}}{\bar{\gamma}_A^{z_B}} = \ln\frac{\bar{\gamma}_B^{0z_A}}{\bar{\gamma}_A^{0z_B}} + z_A z_B\int_0^{\bar{\theta}_w}\frac{\partial\ln\alpha}{\partial\bar{\theta}_B}d\theta_w \quad \bar{\theta}_B = \text{const},\ \bar{n} = \text{const}, \quad (72)$$

where $\bar{\gamma}_B$ and $\bar{\gamma}_A$ are the activities [activity coefficients] of the counterions in the swollen resin with the ionic composition defined by $\bar{\theta}_A$ and $\bar{\theta}_B$ and $\bar{\gamma}_B^0$ and $\bar{\gamma}_A^0$ are the

¶In some cases a resin of a different chemical type may serve as a reference. If such substitution is permissible, the scope of the osmotic theory becomes wider.

activities [activity coefficients] of the counterions in the dehydrated resin of the same ionic composition.

The integral in Eqn. (72) may be transformed using the rule governing the differentiation of a definite integral with respect to a parameter and also Eqn. (9):

$$\ln\frac{\bar{\gamma}_B^{z_A}}{\bar{\gamma}_A^{z_B}} = \ln\frac{\bar{\gamma}_B^{0z_A}}{\bar{\gamma}_A^{0z_B}} + z_A z_B \frac{1}{RT}\frac{\partial\left(\frac{\Phi_{sw(n_w)}}{n}\right)}{\partial\bar{\theta}_B}\bigg|_\alpha - \frac{\partial\bar{\theta}_w}{\partial\bar{\theta}_B}\bigg|_{\bar{a}_w} \cdot \ln\bar{a}_w z_A z_B \,. \quad (73)$$

On substituting Eqn. (73) in the expression

$$-RT\ln\tilde{K}_B^A = -RT\ln K_B^A + RT\ln\frac{\bar{\gamma}_B^{z_A}}{\bar{\gamma}_A^{z_B}} \quad (74)$$

we have the following equation for $\tilde{K}_B^A$:

$$-RT\ln\tilde{K}_B^A = -RT\ln K_B^A + RT\ln\frac{\bar{\gamma}_B^{0z_A}}{\bar{\gamma}_A^{0z_B}} + z_A z_B\Delta\Phi_{sw} - RT z_A z_B\frac{\partial\bar{\theta}_w}{\partial\bar{\theta}_B}\bigg|_\alpha \ln\alpha, \quad (75)$$

where $\Delta\Phi_{SW}$ is the differential free energy of swelling during ion exchange [$\Delta\Phi_{SW} = \partial(\Phi_{SW}/n)/\partial\theta_B|_\alpha$]. The term $(\partial\theta_W/\partial\theta_B)\ln\alpha$ becomes zero when ion-exchange equilibrium in an infinitely dilute solution is considered ($\alpha = 1$). In more concentrated solutions it remains small. This term takes into account the deviation of the state of water in the system from its standard state. $\Delta\Phi_{SW}$ is calculated from isopiestic data for the cross-linked resin at several ionic compositions. It is noteworthy that in Eqn. (75) the term $RT\ln(\bar{\gamma}_B^{0z_A}/\bar{\gamma}_A^{0z_B})$ takes into account the interaction effects in the absence of solvent in the resin, while the term $[\Delta\Phi_{SW} - RT\ln\alpha(\partial\bar{\theta}_W/\partial\bar{\theta}_B)_\alpha] = \Delta\Phi_S$ represents the change in all interactions due to the solvent. In order to find the term $RT\ln(\bar{\gamma}_B^{0z_A}/\bar{\gamma}_A^{0z_B})$, we shall examine the state of the dehydrated resin of mixed ionic composition. This can be regarded as a two-component system, i.e. we have

$$\bar{n}_A\, d\ln\bar{\gamma}_A^0 + \bar{n}_B\, d\ln\bar{\gamma}_B^0 = 0 \,. \quad (76)$$

This equation will be solved simultaneously with the differential of Eqn. (75):

$$d\ln\bar{\gamma}_B^0 = -\frac{\bar{\theta}_A}{z_A}d\ln\tilde{K}_B^A - \frac{z_B\bar{\theta}_A}{RT}d\Delta\Phi_s \,, \quad (77)$$

$$d\ln\bar{\gamma}_A^0 = \frac{\bar{\theta}_B}{z_B}d\ln\tilde{K}_B^A + \frac{z_A\bar{\theta}_B}{RT}d\Delta\Phi_s \,. \quad (78)$$

When the dehydrated monoionic forms of resins are chosen as standard states (here we shall use a symmetrical comparison system [126]), we obtain

$$\lg\bar{\gamma}_B^0 = -\frac{\bar{\theta}_A}{z_A}\ln\tilde{K}_B^A(\theta_A) - \int_1^{\bar{\theta}_B}\frac{\ln\tilde{K}_B^A}{z_A}d\theta_B - \frac{z_B\bar{\theta}_A}{RT}\Delta\Phi_s - \frac{z_B}{RT}\int_1^{\bar{\theta}_B}\Delta\Phi_s\, d\theta_B, \quad (79)$$

$$\lg\bar{\gamma}_A^0 = \frac{\bar{\theta}_B}{z_B}\ln\tilde{K}_B^A(\theta_A) - \int_0^{\bar{\theta}_B}\frac{\ln\tilde{K}_B^A}{z_B}d\theta_B + \frac{z_A\bar{\theta}_B}{RT}\Delta\Phi_s - \frac{z_A}{RT}\int_0^{\bar{\theta}_B}\Delta\Phi_s\, d\theta_B \,. \quad (80)$$

Substitution of Eqns. (79) and (80) in Eqn. (75) yields

$$-\Delta\Phi^0 = RT\ln K_B^A = RT\int_0^1\ln\tilde{K}_B^A\, d\theta_B + z_A z_B\int_0^1\Delta\Phi_s\, d\theta_B \,. \quad (81)$$

At equilibrium in very dilute solutions

$$-\Delta\Phi^{0*} = RT\ln K_B^A = RT\int_0^1\ln\tilde{K}_B^A\, d\theta_B + z_A z_B[\Phi_{sw}(\theta_B=1) - \Phi_{sw}(\theta_B=0)] \,. \quad (82)$$

Thus when dehydrated monoionic forms are chosen as standard states, the contribution of the solvent to selectivity is proportional to the difference between the free energies of swelling of the resins in the pure monoionic forms. Table 4 lists the thermodynamic quantities associated with the exchange of triethylbenzylammonium and sodium ions on KU-1 and Dowex-50 × 2 resins, from which it is evident that, with this method of calculation, the standard free energy of ion exchange becomes more negative. This increase is necessary to compensate the thermodynamically unfavourable effect involving the displacement of the solvent from the resin during ion exchange.

Table 4. Thermodynamic functions of swelling and the exchange of triethylbenzylammonium (TEBA) and Na^+ ions on Dowex-50 and KU-1 resins.

	θ_{TEBA}	Φ_{sw}/n, kcal equiv.$^{-1}$	$\Delta\Phi_{sw}$, kcal equiv.$^{-1}$	$\tilde{\tilde{K}}^{Na}_{TEBA}$	$\ln K^{Na}_{TEBA} = \int_0^1 \ln\tilde{\tilde{K}}^{Na}_{TEBA}\, d\theta_{TEBA}$	$\Delta\Phi^0 = -RT\ln K^{Na}_{TEBA}$, kcal equiv.$^{-1}$	$\Delta\Phi^* = \Delta\Phi^0 + \Phi_{sw}[\theta_{TEBA}=1] - \Phi_{sw}[\theta_{TEBA}=0]$
Dowex-50 × 2	0	4.7	4.0	—			
	0.14	4.2	2.4	7.4			
	0.23	4.1	1.2	5.8	1.7	−1.0	−2.0
	0.48	3.9	0.6	3.6			
	0.95			2.0			
	1.0	3.7	0.3				
KU-1	0	8.7	7.5	—			
	0.15	7.7	6.0	450			
	0.32	6.8	4.5	230	5.6	−3.4	−7.0
	0.40	6.6	2.8	180			
	0.95			20			
	1.0	5.1	2.2	—			

Note. The values of $\tilde{\tilde{K}}^{Na}_{TEBA}$ at $\theta_{TEBA} = 0$ and $\theta_{TEBA} = 1$ were obtained by extrapolation. It was assumed that $\gamma_{TEBA}/\gamma_{Na} = 1$ under the experimental conditions (μ = 0.1 M).

Thus the lowering of the selectivity with respect to ions on reduction of the degree of cross-linking of resins is determined to a large degree by the thermodynamically unfavourable contraction of the resin and the decrease of its solvent content, which are in many cases larger for more readily swelling sorbents. We arrived at similar conclusions in the study of other systems [122,123]. We may note that the use of Eqns. (75), (79), and (80) permits the calculation of $\tilde{\tilde{K}}^A_B$ from isopiestic data for the given resin having several compositions and also from the ion-exchange isotherm for the resin. It is, however, possible to reduce the calculation of $\tilde{\tilde{K}}^A_B$ for a cross-linked resin to a calculation from isopiestic data for another resin of a different type with a different amount of cross-linking agent, since there exists the following expression relating the values of $\Delta\Phi_S$ for resins cross-linked to a different extent [125]:

$$\Delta\Phi_s - \Delta\Phi_s(\text{ref.}) = \int_0^{\theta_w}\frac{\partial(\pi v_w)}{\partial\theta_B}d\theta_w + RT\int_{\theta_w(\text{ref.})}^{\theta_w}\frac{\partial\ln\alpha}{\partial\theta_B}d\theta_w \,. \quad (83)$$

For systems in which $\pi = F(V_e)$ [see Eqn. (53)],

$$\Delta\Phi_s - \Delta\Phi_s(\text{ref.}) \simeq \pi\Delta v_l + RT\int_{\theta_w(\text{ref.})}^{\theta_w}\frac{\partial\ln\alpha}{\partial\theta_B}d\theta_w \,. \quad (84)$$

If it is assumed that the ion-exchange equilibrium constant K^A_B is independent of the degree of cross-linking [Eqn. (52) of the osmotic theory is based on a similar assumption], then, combining different expressions, it is possible to obtain an equation for the determination of $\tilde{\tilde{K}}^A_B$ for the

given resin from $\approx{}^{A}_{B}K$ (ref.) for the reference resin from its isopiestic data at several compositions and the maximum swellability of the given resin at several compositions. Thus, within the framework of the formal thermodynamic method too, it is possible to calculate independently the apparent ion-exchange equilibrium constants.

The structural characteristics of ion-exchange resins are shown in particular in the phenomena of the steric inaccessibility and the screening of sorption centres, while the hydration properties of resins also have a significant influence on their selectivity with respect to different ions. Systematic accumulation of experimental data on the relation between the selectivity and swellability of ion-exchange resins of different structures is necessary for further development of theories in this field.

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Institute of Macromolecular Compounds, Leningrad

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Methods of Measurement of Small Separation Coefficients

D.A.Knyazev, Ya.D.Zel'venskii, N.F.Myasoedov, and G.G.Filippov

Methods of measurement of small separation coefficients are reviewed. The methods cover the whole range of separation conditions used in practice. Their main characteristics are tabulated, and each method is discussed mathematically in detail. The limitations of their applicability are considered, together with the magnitude of likely sources of error. The preferred regions for the various methods are identified, specific features of the experimental procedure are listed, and the apparatus is described. Most of the examples are taken from papers on the separation of isotopes, because this work demands the highest precision and reliability in the measurement of separation coefficients, and offers the widest choice of published results. 87 references.

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I. INTRODUCTION

A new and fast-developing area in chemical engineering and in preparative and analytical chemistry is concerned with the separation of mixtures of closely similar constituents. Systems of this type include many mixtures of biologically important substances, such as mixtures of aminoacids and of polysaccharides, mixtures of members of genetic and of homologous series, of polymers, of isomers, of isotopes, of rare earths, etc., all of which are notoriously difficult to separate.

The thermodynamic properties of these compounds are usually very similar over a wide range of conditions and for the most diverse chemical forms and states of aggregation into which they can be transformed. Hence the difficulty experienced in separating them. The corresponding separation processes (or reactions) are characterised by single-stage separation factors close to unity, and therefore methods which automatically perform a multiplicity of separation acts are used to prepare the pure compounds. The most important of these methods are fractional distillation, extraction, chromatography, fractional crystallisation, and their many variants.

The rational application of these processes demands a knowledge of the separation coefficients of the components in the particular physicochemical systems under study. This is clearly recognised in the area of isotope and rare-earth separation, and one of the main research activities with these materials is a search for systems and conditions giving rise to significant or acceptable separation coefficients. On the other hand, in biochemistry and related areas the approach tends to be empirical, and preliminary studies of the magnitude of the elementary act are usually omitted. There can be no doubt that a more quantitative approach is needed in this area also, involving a sufficiently accurate analytical assessment of the efficiency of the process under study.

The methods most frequently used to determine separation coefficients are listed in Table 1 together with a brief summary of their main characteristics.

Definitions

The term "small separation coefficient" is used to denote values close to unity, but the extent of approach to unity is not defined. It may be convenient to include all value not exceeding two, because their measurement requires the use of high-precision methods such as those discussed in this review. These special methods must be used also when the separation coefficients being measured differ fractionally from unity: hence there is a similarity between very small separation coefficients and those of the order of two.

Separation coefficient. Given two chemical forms, phases, or states A and B between which the components i and l can undergo chemical or phase exchange, the separation coefficient α_{il} which characterises the exchange of the components is defined by

$$\alpha_{il} = \frac{[x_i]_A}{[x_l]_A} \cdot \frac{[x_l]_B}{[x_i]_B}$$

where $[x_i]_A$, $[x_l]_A$, $[x_i]_B$, and $[x_l]_B$ are the mole fractions of the components in forms A and B respectively. Both equilibrium and non-equilibrium process can be characterised by means of α. In the former case the concentrations must meet the usual requirements of dynamic equilibrium. The following terms are often used synonymously with separation coefficient: single-stage separation factor, equilibrium constant, relative fugacity.

The *enrichment coefficient* is defined by the expression

$$\varepsilon_{il} = \alpha_{il} - 1.$$

The value of ϵ for mixtures which cannot be easily separated is often much smaller than unity, and in these cases the separation obtainable in the system is best described in terms of ϵ. This quantity will therefore be used most frequently in what follows, and the precision of the experimental methods will be referred to it.

Table 1.

Method / Characteristics	Single contact	Differential	Multistage extraction	Rayleigh's continuous extraction	Elution chromatography	Rectangular cascade	Craig counter-current extraction
Field of application	Heterogenous phase exchange	Phase exchange	Heterogeneous exchange	Heterogeneous and homogeneous phase exchange	Heterogeneous exchange	Heterogeneous phase exchange	Heterogeneous exchange
Lowest measurable values	0.03	0.005	0.002	0.002	0.0002	0.01	0.01
Amount of mixture (mmole) needed	0.1—10	5—20	10^2—10^4	10^2—10^4	10^{-2}—10^{-1}	10^4	10^{-1}—1
Number of precision analytical determinations per measurement	2	0	2	2	10	2—10	10
Duration of experiment ignoring preparative stages	minutes to hours	minutes to hours	over an hour	hours	hours to days	hours to days	hours to days

Degree of separation. The efficiency of any separation process operated in an apparatus designed to maximise the effect of single-stage separation is characterised by the degree of separation, which is generally referred to the initial and the final state of the product, to some fixed points in the apparatus, and to a specified time:

$$Q_{il} = \frac{[x_i]_1}{[x_l]_1} \cdot \frac{[x_l]_2}{[x_i]_2}.$$

The time parameter needs to be considered only in special cases, and is therefore often omitted in the definition of Q_{il}.

II. SINGLE CONTACT METHOD

The field of application of the single contact method embraces all types of physicochemical equilibrium. The method is used to measure small coefficients when only a preliminary assessment is required, or when the result is sufficiently different from unity to ensure that the desired precision is achieved without resorting to multiple separations. In this case the problem consists in measuring the concentrations of the materials in the phases or forms to be equilibrated. The measurement accuracy can be improved by a number of simple procedures, by the use of special analytical methods, or by taking a large number of measurements and applying a standard statistical analysis.

If a method for measuring the difference in concentration of components i and l in the forms to be equilibrated is available, and the concentration of the components in the initial mixture is accurately known, the coefficient ϵ_{il} for the multicomponent mixture can be determined from the expression

$$\varepsilon_{il} = \frac{x_l^0 \Delta i - x_i^0 \Delta l}{(x_l^0 - \theta \Delta l)\left[x_i^0 - (1-\theta)\Delta l\right]} \qquad (1)$$

where $\Delta i = x_1 - y_1$, $\Delta l = x_1 - y_1$, x_1^0 and x_1^0 are the initial concentrations of the components i and l, and θ is the fraction of the material in form B, for which the concentrations are denoted by the symbol y.

In the case of a binary mixture the expression can be simplified, and only the concentration difference Δ_1 of the first component and the quantity θ need to be measured:

$$\varepsilon = \frac{\Delta_1}{(1 - x_1^0 - \theta\Delta_1)(x_1^0 - \Delta_1 - \theta\Delta_1)}. \qquad (2)$$

It is often possible and desirable to contact small amounts of form B with large amounts of form A. In this case $\theta \to 0$, and the measurement of ϵ involves simply a measurement of the difference Δ_1:

$$\varepsilon = \frac{\Delta_1}{(1 - x_1^0)(x_1^0 - \Delta_1)}. \qquad (3)$$

It is evident from the above expressions that, other conditions being equal, the value of Δ_i and Δ_l increases with x_l and x_i. Since the accuracy of the measurement of ϵ is determined by the accuracy with which Δ can be measured, conditions tending to maximise Δ should obviously be chosen if possible.

The relationship between the accuracy of the measurement of ϵ and that of the analytical method used is illustrated by the highly precise work of Boato and coworkers [1], who studied the separation of nitrogen, oxygen, and noble gas isotopes by liquid–vapour phase exchange. Due to the small error of their mass-spectrometric method of analysis, they were able to measure ϵ to the fourth decimal place.

The experimental requirements of the single contact method are determined primarily by the nature of the separation process under study. In the case of equilibrium separation processes the requirements coincide with the well known conditions for the achievement of true dynamic equilibrium. The most important of these is a correct choice of equilibration time, which implies a fairly precise knowledge of the kinetics of the process. The equilibrium criterion most commonly adopted is agreement between

values of ϵ obtained after long and significantly different contact times, or after approaching equilibrium from different directions.

In the study of non-equilibrium separation processes, on the other hand, we must ensure that the reaction can proceed in one direction only. This is most frequently achieved by working on the initial portion of the relaxation curve or under artificially maintained quasi-stationary conditions. For example, in high-vacuum distillation studies the molecules emitted from the liquid at a given temperature must be condensed at a very much lower temperature to ensure that the backward flow of molecules is negligibly small.

The apparatus required for the single contact method is usually fairly simple. Typically, temperature-control and stirring facilities are needed. The apparatus and techniques used in extraction, crystallisation, and ion exchange studies have been discussed in recent review articles [2-4]. The monograph by Hala and coworkers [5] gives an extensive and detailed review of the experimental assemblies used to study liquid–vapour equilibria. Apparatus based on Bushmakin's design [6] is most commonly used in Soviet laboratories investigating liquid–vapour equilibria. Combs and coworkers have proposed a contact apparatus which ensures complete saturation of the carrier gas by the vapour. More complicated designs are used in studies of non-equilibrium processes or under extreme experimental conditions. For example, the apparatus for studying separation by high-vacuum distillation has some unusual design features [8].

III. DIFFERENTIAL METHOD

The differential method [9,10] applies only to the liquid–vapour phase transition in binary mixtures, since it relies on the difference in equilibrium vapour pressure of two liquids at the same temperature, or alternatively on the difference in boiling point at a fixed pressure. There is a simple relationship between these easily measurable quantities and the separation coefficient, due to the similarity in thermodynamic properties of substances which are difficult to separate, which ensures that liquid and gaseous mixtures of this type are thermodynamically ideal. At a constant temperature, the vapour pressure of an ideal binary liquid mixture is the sum of two partial pressures which are themselves determined (according to Raoult's law) by the composition of the liquid mixture in equilibrium with the vapour:

$$P = P_1^0 x_1 + P_2^0(1 - x_1); \quad y_1 = \frac{P_1^0 x_1}{P}; \quad y_2 = 1 - y_1 = \frac{P_2^0(1 - x_1)}{P}. \quad (4)$$

The separation coefficient of the equilibrium distillation process is

$$\alpha = \frac{y_1}{y_2} \cdot \frac{x_2}{x_1} = \frac{P_1^0}{P_2^0} = 1 + \frac{P_1^0 - P_2^0}{P_2^0}. \quad (5)$$

The measurement of α involves merely a determination of the difference in vapour pressure between the two liquids (Δp) [9,11] and of the absolute vapour pressure of one of the liquids (isothermal variant). The same problem can be solved indirectly by measuring the difference in boiling point between the liquids as a function of pressure, and also the vapour pressure of one of the liquids as a function of temperature (isobaric variant [10]). The method can be used also to test the ideality of mixtures [12] or to study the variation of α with composition of the liquid phase [13]. In this case the vapour pressure of a series of mixtures is measured with respect to that of a standard mixture, or of a pure component. *A priori* evidence of the ideality of the mixture is often available, as in the case of mixtures of isotopic forms, of isomers, or of near homologues. In these systems, a relative measurement of the vapour pressure of two mixtures of known and different composition is sufficient to determine α. The quantities P_1^0 and P_2^0, and therefore also α, are obtained by solving the simple system of simultaneous equations

$$P' = P_1^0 x' + P_2^0(1 - x')$$

$$P'' = P_1^0 x'' + P_2^0(1 - x''). \quad (6)$$

The same information can be obtained by measuring differences in boiling point. The isobaric (ebullioscopic) method involves the determination of Δt as a function of total pressure in order to arrive ultimately at expressions (4)–(6). The mathematical transformation is performed graphically or by means of empirical expressions.

These two methods offer a number of advantages over alternative methods of measuring small values of ϵ. The apparatus and procedure are relatively simple, no special analyses are required, the parameter α can be measured over a very wide range of temperatures and pressures, and as a function of composition, and lastly very small amounts of material are needed for the measurement, and can be recovered. The main drawback of the method is the requirement of extreme purity, since both modifications of the method are very sensitive to the presence of volatile impurities. The isothermal modification has the advantage that measurements of Δp as a function of temperature are not normally required, but there is little to choose between the two variants when measurements of α are required over a fairly wide range of conditions.

The method has become generally used [9-11,13-16] as one of the most reliable procedures for measuring α in isotopic mixtures. It has also been applied to mixtures of isomers [12] and to non-ideal mixtures [13].

The main parts of an isothermal apparatus for the measurement of α by the differential method are a manometer to indicate the pressure of the substances or mixtures to be compared, a differential manometer, a temperature control system, a vacuum system, and a gas-handling system (Fig. 1). In the best designs, the manometers are in the form of holes drilled through metal blocks of high thermal conductivity in order to minimise temperature differences and to increase the thermal inertia of the system [14]. Constructions have been described which allow the temperature to be controlled to 0.0001° at the −195°C level, and to 0.01° at +370°C. [15,15a,16]

Combs and coworkers [7] used an unusual form of the differential isothermal method. A stream of carrier gas is led alternatively through thermostatted saturators containing the liquids to be compared and through desorbers. The design of the saturators and desorbers ensures quantitative saturation and scrubbing: the vapour pressure of the liquids is measured by the increase in weight of the desorbers.

Isobaric assemblies are based on ebulliometers essentially similar in design to the device described by Hala and coworkers [5]. The only difference is that two ebulliometers are used together, in a common manometric system.

The accuracy of the method is controlled by the following factors: the absolute difference in vapour pressure or in boiling point of the substances being compared, the precision of the equipment used to measure Δp or Δt, the

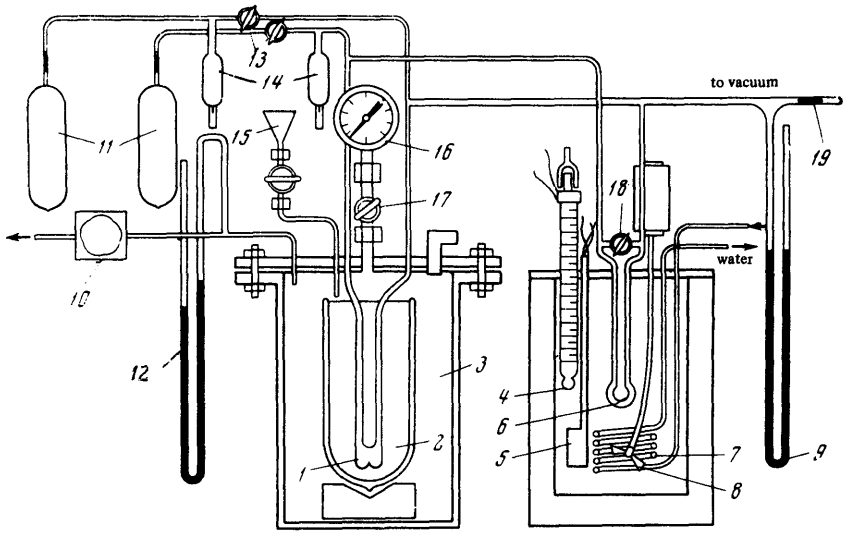

Figure 1. Apparatus for measuring α by the differential method: *1*) bulb for experimental liquid; *2*) Dewar vessel; *3*) metal jacket; *4*) contact thermometer; *5*) heater; *6*) differential manometer; *7*) cooling coil; *8*) stirrer; *9*) mercury manometer; *10*) needle valve; *11*) storage bulbs; *12*) vacuum gauge; *13*) taps; *14*) sample holders; *15*) filler tap and funnel; *16*) manometer; *17*) valve; *18*) manometer bypass valve; *19*) vacuum seal-off point.

grade of the thermostat or manostat, and the purity of the compounds. Differential manometers are usually read with a cathetometer, which allows Δp to be measured with a precision of 0.01 mmHg. In principle, therefore, it is possible to measure ϵ with an error of a few units in the fifth decimal place. The isobaric method is more complicated and not so widely used. It requires specially calibrated resistance thermometers and a special electrical measuring bridge. The measurement accuracy can be as high as 0.001°, and the error in ϵ can be of the same order as in the isothermal variant.

Purity of the samples to be compared is the overriding condition for a successful and accurate determination of ϵ. To achieve the requisite purity, a complex sequence of purifications is often required, involving the development of special procedures and apparatus.

IV. MULTISTAGE EXTRACTION (CONDENSATION) METHOD

The multistage extraction method consists in the gradual enrichment (with respect to one or several components) of one of the two forms, achieved by simple repetition of a single-stage separation procedure. The experimental pair of chemical forms A and B is brought into dynamic equilibrium, the mixtures in form A and B respectively being taken in comparable amounts. Forms A and B are separated before the establishment of equilibrium: one of these forms becomes enriched with respect to one of the components, and vice versa. The entire operation (equilibration and separation of the forms) is termed a condensation stage. After the first stage, some fraction of form (or phase) A is converted into form (or phase) B by chemical or thermal methods. The sample of form B thus obtained, and the remainder of form A, are then brought into dynamic equilibrium once again, and forms A and B are again separated. As a result of the second stage, form A is enriched still further in the given component, and the subsequent "condensation" stages of form A raise the level of separation of the components to the point when the separation of all the components becomes accurately measurable. The degree of separation is measured with respect to the concentration of the components in form A after the first "condensation" stage. The amounts of forms A and B are controlled at each stage at the moment of separation. It is often desirable to condense both forms A and B: this two-fold condensation procedure yields two final samples A_f and B_f, enriched in different components. By comparing the degrees of separation of these two samples it is possible to double the accuracy of the determination of the separation coefficient.

The efficiency of the condensation process depends on two factors: the number of separation stages and the distribution of the degree of condensation over the stages. The degree of condensation of one stage is defined as the reciprocal of the recovery θ, i.e. the ratio of the amount of the form to be extracted obtained at the stage $(j-1)$ to the amount of the same form obtained at the jth stage: $L_j = G_{j-1}/G_j$. Katal'nikov and Boreskov [17] studied this problem and showed that for a given number of stages n and a given total degree of condensation ($L_\Sigma = \Pi_i L_i$) the maximum separation is obtained for equal degrees of condensation at all stages: $L_j = \sqrt[n]{L_\Sigma}$. They also showed that for a given degree of condensation the separation increases approximately exponentially with the number of stages: hence it is rational to choose a relatively small number of condensation stages (Fig. 2).

The same authors [17] proposed an accurate graphical method of calculation of small values of ϵ from the results of multistage extraction experiments for binary mixtures. This method is similar in many ways to the familiar

procedure for computing the number of theoretical plates. It enables the concentration of one of the components to be very simply computed after any number of extraction stages, whether one form is being extracted or both simultaneously. However, a knowledge of α is needed before the graphical method can be applied. The calculation is therefore made by trial and error, and the correlation between ϵ and Δx_{Σ} is used to give a more accurate value of ϵ.

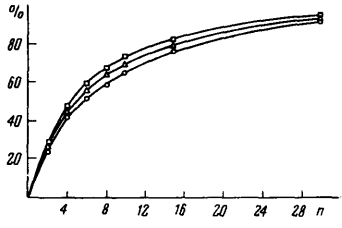

Figure 2. Ratio $\frac{\ln Q_{m.e.}}{\ln Q_{c.e.}}$, expressed as %, against number of condensation steps n. $Q_{m.e.}$ is the separation of the components of a binary mixture by the multistage extraction method, $Q_{c.e.}$ is the separation of the same mixture by Rayleigh's continuous extraction method. Circles for $\alpha = 1.001$; triangles for $\alpha = 1.010$; squares for $\alpha = 1.100$.

Kuznetsova and coworkers [18] proposed an analytical expression for calculating $\epsilon \ll 1$ directly from multistage extraction results (n stages) assuming an equal degree of condensation for each stage:

$$\alpha = \frac{\sqrt[n]{\frac{x_0}{x_n}} - \theta}{1 - \theta}. \qquad (7)$$

This equation is not entirely satisfactory, because it can be applied only at low concentrations of one component. Outside the low concentration region the relative error in ϵ becomes large, since it is directly proportional to x_0.

The equation proposed by Mikhailichenko and Shcheglov [19] is free from the last two drawbacks, but it also applies only for $\epsilon \ll 1$:

$$\varepsilon = \frac{x_n - x_0}{x_0(1 - x_0)\left(n - \sum_{j=1}^{n} Q_j\right) - x_0(x_n - x_0)}. \qquad (8)$$

An analogous expression for an n-component mixture ($\epsilon_{ek} \ll 1$) was obtained by Knyazev and Bantysh [20]:

$$\varepsilon_{ek} = \frac{\ln Q_{ek}}{n - \sum_{j=1}^{n} \Theta_j - \sum_{l=k}^{m} x_l}. \qquad (9)$$

Hence ϵ_{ek} is the enrichment coefficient, referred to some reference component k, Q_{ek} and Q_{jk} are the separations of components j and e with respect to the reference component. When the separation coefficients are significantly different from unity ($\epsilon \leqslant 0.2$) this expression becomes inaccurate. In these cases systems of equations of the following form must be used:

$$\ln Q_{ek} = \varepsilon_{ek} \sum_{j=1}^{m} \frac{1 - q_j}{1 + q_j \sum_{i=1}^{n} \varepsilon_{ik} y_{ij}} - \frac{\varepsilon_{ek}^2}{2} \sum_{j=1}^{m} \frac{(1 - q_j)^2}{\left(1 + q_j \sum_{i=1}^{n} \varepsilon_{ik} y_{ij}\right)^2}. \qquad (10)$$

The system can be solved by successive approximation; the first approximation for ϵ_{ek} can be the values given by Eqn. (9), and $\sum_{i=1}^{n} \epsilon_{ik} y_{ij}$ for each stage can be evaluated with sufficient accuracy by assuming that this sum is linear in the number of stages j. When the assumption that the quantity ϵ_{ek} is linearly related to some known parameter of the component e can be justified, measurement of all the Q_{ek} becomes superfluous, and only the separations of the two "extreme" (most easily separable) components needs to be measured. For example, in multicomponent isotopic mixtures ϵ_{ek} varies linearly with the isotopic mass M_e:

$$\varepsilon_e = \varepsilon_0 (M_e - M_k).$$

By using expressions of this type Eqn. (10) can be rewritten

$$\varepsilon_0 = \frac{\ln Q_{ek}}{(M_e - M_k)\left(m - 1 - \sum_{j=2}^{n} q_j\right) - \ln Q_{ek} \sum y_{i0} (M_e - M_k)}. \qquad (11)$$

The method has been most generally applied to measurements of the separation coefficients of isotopes. Many systems involving heterogeneous isotope exchange have been investigated, including solution–sorbent, solution–crystals, and liquid–liquid systems [21–26]. The main attraction of the method is that it can be applied without special equipment, using only the apparatus needed to measure ϵ by the single contact method.

V. RAYLEIGH'S CONTINUOUS EXTRACTION METHOD

Rayleigh's method [27,28], also known as the continuous extraction or residue concentration method, is most commonly applied in distillation theory. It does not suffer from any of the limitations of the separation methods discussed above, and is undoubtedly applicable to the most diverse systems even though it is mostly used in studies of liquid–vapour equilibria at present.

The main difficulty associated with the Rayleigh method is the need to observe two sets of conditions at the same time: on the one hand, the concentrated (extracted) form must be free from concentration gradients, and on the other hand the concentration of this form and the take-off of the resulting new form must be carried out in infinitesimally small amounts. It is not difficult to comply with these conditions in simple distillation, but the study of other separation processes by this method is often complicated by the properties of the forms under investigation, or may require special experimental techniques.

The advantages of the method include: relatively high separation, allowing the separation coefficients to be measured accurately; non-equilibrium as well as equilibrium processes can be investigated; short experimental time (in the study of fast processes); relatively simple apparatus.

Since the method can be applied to a wide variety of separation processes, we shall describe it in the most general terms. Let the system have n components, and assume that each component can exist in two states (1 and 2). At the beginning of the experiment the whole of the mixture (G_0) is in state 1. We assume that the mixture can be transferred by some method from state 1 to state 2 in infinitesimally small increments dG, and that a method for instantaneously removing the mixture in state 2 is available. We further assume that the transition of an

arbitrary component (i) from state 1 to state 2 occurs with probability $P_i x_i$, where P_i is in general some function of the concentration of all the components in the mixture (x_i) in state 1, and also of the experimental conditions. Lastly, let the concentrations of the substances in the mixture in state 1 be described by their mole fractions x_i, and those in state 2 by their mole fractions y_i. It can easily be shown that the following relationship exists between the quantities x_i, y_i, P_i, dG_i, and dG:

$$\frac{dG_i}{dG} = y_i = P_i x_i = P_i \frac{G_i}{G}. \qquad (12)$$

Dividing Eqn. (12) for component i by the analogous equation for component j, we obtain after some simple transformations

$$d \ln G_i = \frac{P_i}{P_j} d \ln G_j. \qquad (13)$$

The probability functions P_i and P_j depend on a number of factors, including first of all some specific properties of states 1 and 2. For example, we may be considering two processes as closely related as equilibrium distillation and vacuum distillation of liquid mixtures. In the former, the probabilities of $1 \rightarrow 2$ transitions will be determined by temperature and by the difference between the thermodynamic properties of the components in the different states; in the latter, they will be determined by temperature and by the molecular weight of the components. Furthermore, pressure, reactions with extraneous chemical compounds, concentration gradients, etc. may also affect the values of P_i and P_j. Lastly, the dependence of P_i and P_j on the concentration of the components i and j, and of other components undergoing the transition $1 \rightarrow 2$, should in general be considered. For a Rayleigh process in which all conditions except the concentrations of the i and j components are kept constant, integration of Eqn. (13) is possible only if the functions P_i and P_j are available in an explicit form. However, at least as regards thermodynamic separation processes, near-unity separation coefficients can be taken as evidence that the mixtures under study are close to ideality. This implies constancy of P_i and P_j (and even more so of their ratio P_i/P_j). Since the separation coefficient can be accurately measured with relatively small concentration changes, the assumption is fully justified. Thus, if the above assumptions hold true,

$$\frac{P_i}{P_j} = \frac{y_i}{x_i} \cdot \frac{x_j}{y_j} = \alpha_{ij} = \text{const}.$$

After integration we have

$$\ln \frac{G_{i_0}}{G_i} = \alpha_{ij} \ln \frac{G_{j_0}}{G_j}. \qquad (14)$$

Transformation of Eqn. (14) gives the following forms of the Rayleigh equation:

$$\ln Q_{ij} = \ln \frac{x_{i_0}}{x_i} \cdot \frac{x_j}{x_{j_0}} = \ln \frac{y_{i_0}}{y_i} \cdot \frac{y_j}{y_{j_0}} = \varepsilon_{ij} \ln \frac{G_{j_0}}{G_j}. \qquad (14a)$$

$$\ln Q_{ij} = \varepsilon_{ij} \left[\ln \frac{G_0}{G} + \ln \frac{x_{j_0}}{x_j} \right] = \varepsilon_{ij} \left[\ln \frac{G_0}{G} + \ln \frac{y_{j_0}}{y_j} \right]. \qquad (14b)$$

The approximate form

$$\ln Q_{ij} = \varepsilon_{ij} \ln \frac{G_0}{G}, \qquad (14c)$$

can be used if $\epsilon_{ij} \ll 1$.

For the case of two-component systems, Eqn. (14) can be converted into well known, precise expressions in which the ratio of concentrations of component 1 is presented[27] as a function of the degree of condensation[25]:

$$\ln \frac{x_{10}}{x_1} - \alpha \ln \frac{1 - x_{10}}{1 - x_1} = (\alpha - 1) \ln \frac{G_0}{G}.$$

$$Q = \frac{x_{10}}{x_1} \cdot \frac{1 - x_1}{1 - x_{10}} = \left(\frac{G_0}{G} \right)^{\alpha - 1} \left(\frac{1 - x_{10}}{1 - x_1} \right)^{\alpha - 1}. \qquad (15a)$$

For $\epsilon \ll 1$ we have

$$\ln \left(\frac{x_{10}}{1 - x_{10}} \cdot \frac{1 - x_1}{x_1} \right) = \ln Q \cong \varepsilon \ln \frac{G_0}{G}, \qquad (15b)$$

and with the additional condition $x_{10} \ll 1$, leading to $\alpha = y/x$, we obtain

$$\ln Q \ln \frac{x_{10}}{x_1} \approx \ln \frac{y_{10}}{y} \approx \varepsilon \ln \frac{G_0}{G}. \qquad (15c)$$

It is evident from Eqns. (14), (14a), and (15c) that measurement of α_{ij} requires only a knowledge of the initial and the final amount of material in the mixture in state 1 (to be condensed), as well as of the concentrations of the components of interest at those times. In other words, these quantities need to be known, in principle, before the beginning of the process and at any one time during the process. In this sense, Eqn. (14) and Eqns. (14a)–(14c) are equivalent. However, they are far from being equivalent as regards the accuracy with which $(\alpha_{ij} - 1)$ can be calculated. As can readily be shown, the relative errors in the calculation of ϵ_{ij} by Eqn. (14) and by the widely used Eqn. (14c) are given, respectively, by the expressions

$$\frac{\Delta \varepsilon_{ij}}{\varepsilon_{ij}} = \frac{\Delta \ln Q_{ij}}{\ln Q_{ij}} + \frac{\Delta \ln z}{\ln z} \qquad (16a)$$

$$\frac{\Delta \varepsilon_{ij}}{\varepsilon_{ij}} = \frac{\Delta \ln Q_{ij} + 2 \Delta \ln z}{\ln Q_{ij}}. \qquad (16b)$$

Since Q_{ij} is usually close to unity, the second term in the numerator of the right-hand side of Eqn. (16b) contributes very significantly to the overall error, whereas the second term in the right-hand side of Eqn. (16a) is small because of the magnitude of $\ln z$. Because Q_{ij} does not differ much from unity and is therefore difficult to measure accurately, multiple measurements of Q_{ij} and z are desirable. Since samples of the "condensed" state 1 are usually more difficult to remove, and involve a correction for the effective degree of condensation z, it is preferable to analyse the material in the "drawn off" state 2. In the case of simple distillation, for example, vapour samples are usually analysed.

Any method of analysis requires a finite sample of the material to be analysed. It is important to establish the relationship between the size of the sample and the size of the permissible final residue of extracted mixture in state 1. It can be shown that the error arising from the discrepancy between the theoretical concentration (corresponding exactly to G) and the actual mean concentration becomes negligible if the degree of condensation is calculated for a value of G corresponding to the "mean point" of the sample taken off (volume $2\Delta G$). When the degree of condensation is calculated in this way, the relative error in the measurement of concentration becomes

$$\frac{\Delta y}{y} \cong -\frac{(\alpha - 1)}{3} \left(\frac{\Delta G}{G} \right)^3. \qquad (17)$$

Thus, the removal of samples of finite volume does not impose rigid limitations on the size of the minimum permissible final residue. This allows significant degrees of condensation to be achieved without serious error.

Until recently, Rayleigh's method has been applied to the measurement of small separation coefficients when the

process under investigation is not complicated by the presence of extraneous separation processes, and when the experimental arrangements needed to realise the basic conditions of the Rayleigh process are not unduly complex. These requirements are easily met in simple distillation processes, and in particular in the equilibrium distillation of mixtures consisting of members of a series of related compounds or other materials with closely similar properties [29], in the molecular distillation of isotopic mixtures [30], in some isotope exchange processes [31], in electrolytic methods of isotope separation [32,33], and also in separation processes relying on equilibrium crystallisation from aqueous solutions [34].

More recently, Rayleigh's method has been shown to be applicable to the study of homogeneous isotope exchange and exchange in heterogeneous extraction, ion-exchange, and other heterogeneous systems [35-37].

Lastly, the Rayleigh process can be used to study separation phenomena such as the diffusion of gases through porous partitions, diffusion through liquid films, etc.

1. Rayleigh Distillation

Rayleigh's method is used mostly to study separation in liquid–vapour systems, for which the correct experimental conditions have been most accurately identified and suitable apparatus and experimental procedures have been developed. Only the basic features of the method will be discussed in the present review: some of these are general features, others are more specific. Even the latter, however, are almost invariably present (in a modified form) in other separation processes as well.

In the experimental realisation of Rayleigh's method, various specific features of the distillation process itself must be taken into account. Furthermore, the simpler laboratory assemblies invariably present some undesirable aspects which must be minimised. Lastly, some unavoidable phenomena must quantitatively evaluated and allowed for.

1. True liquid–vapour equilibrium occurs when the evaporation and condensation fluxes are equal. Since evaporation of the liquid must proceed at a practically useful rate in the Rayleigh process, this process is a quasi-stationary one, and the separation coefficients obtained can approach the equilibrium values only in the most favourable (or most unfavourable) cases [38,39]. Obviously, the measured coefficients will be closer to the equilibrium values, the smaller the vapour take-off is in relation to the exchange flow of material between liquid and vapour. In practice, the optimum rate of evaporation is found experimentally, by monitoring the dependence of the observed separation coefficient (α) on the evaporation rate. The range of evaporation rates corresponding to a constant value of α is chosen for the experiment. Conversely, in molecular distillation the true value of the separation coefficient can only be obtained in the total absence of vapour condensation. This condition can be met by removing the evaporated material from the vicinity of the liquid as rapidly as possible [30].

2. The application of the integral forms of the Rayleigh equation presupposes constancy of the separation coefficients. As stated above (see p. 571), this in turn implies independence of the separation coefficient upon the composition of the mixture and constancy of temperature. In practice, the process is most frequently applied at constant pressure [29]. As the composition of the liquid phase changes, the boiling point under isobaric conditions also changes. However, near-unity separation coefficients usually imply that the substances to be separated have similar boiling points, so that at moderate degrees of separation isobaric evaporation is a good approximation to isothermal evaporation. This is also true when the components differ significantly in boiling point provided that the measurements are confined to low concentrations of one component. In these cases, the condition of constancy of the separation coefficient is automatically satisfied.

3. It follows from the initial, differential form of the Rayleigh equation (Eqn. (12)) that the composition of the sample must be representative of that of the whole of the condensed phase. From the standpoint of equilibrium and molecular distillation, this implies that the composition of the liquid near the evaporating surface must be identical to the composition at any other point in the liquid phase, i.e. that the liquid phase must be free from concentration gradients. Mechanical stirring is therefore widely used. The stirring conditions depend on the design and type of stirrer, and are chosen empirically. The criterion for satisfactory stirring is independence of the observed value of α upon the intensity of stirring (number of revolutions per minute).

4. The definition of separation coefficient in both equilibrium and molecular distillation implies that the vapour phase must be strictly homogeneous and must not contain any particles of the liquid phase. Since boiling of the bulk liquid usually gives rise to a large amount of spray, the distillation process is usually carried out under conditions approximating to isothermal evaporation from the surface, which imposes severe limitations on the effectiveness of mixing. Stirring helps to avoid overheating of the liquid and to obtain quiet evaporation. However, the intensity of stirring must be kept below the limit at which spray formation sets in.

5. The equilibrium separation coefficient in distillation cannot be measured under conditions leading to multiple separation acts. Hence, vapour condensation and reflux from the vapour to the liquid is permissible only at the main condensation surface. Vapour condensation in the vapour volume and at the walls of the evaporation vessel must be excluded, and hence the vapour and the walls of the evaporator must be kept at a temperature such that condensation is impossible.

6. Evaporation vessels are usually designed (Fig. 3) so that the total volume occupied by the liquid and the vapour phase is constant throughout the experiment. Under these conditions the amount of material in the vapour state at the end of the experiment is comparable with the amount of liquid mixture. Mechanical stirring of the liquid may be supplemented by stirring of the vapour, which is even more effective, since it brings a finite amount of the vapour phase into equilibrium with the liquid rather than an infinitesimally thin layer. Allowing for these conditions [39], the initial differential and the final integral equation for the process should be written in a form which differs substantially from Eqn. (12) and following. Allowing for the volume of the stirred vapour phase leads to the equations:

$$\lg\frac{y_i}{y_f}=\lg\frac{x_i}{x_f}=\frac{\alpha\,(v_v-v_l)}{v_v-\alpha v_l}\cdot\lg\frac{G_i\,(v_v-\alpha v_l)+\varepsilon V}{G_f\,(v_v-\alpha v_l)+\varepsilon V}+\lg\frac{G_f}{G_i} \qquad (18a)$$

$$\lg\frac{x_i}{z_f}=\frac{\alpha\,(v_v-v_l)}{v_v-\alpha v_l}\cdot\lg\frac{G_i\,(v_v-\alpha v_l)+\varepsilon V}{G_f\,(v_v-\alpha v_l)+\varepsilon V}-\lg\frac{G_f\,(v_v-\alpha v_l)+\varepsilon V}{G_f\,(v_v-v_l)}+\lg\frac{G_f}{G_i} \qquad (18b)$$

$$\lg\frac{x_i}{x_f}=\frac{\alpha\,(v_v-v_l)}{v_v-\alpha v_l}\lg\frac{\alpha V+g_{li}\,(v_v-\alpha v_l)}{\alpha V+g_{lf}\,(v_v-\alpha v_l)}+\lg\frac{V+g_{lv}\,(v_v-v_l)}{V+g_{lf}\,(v_v-v_l)}. \qquad (18c)$$

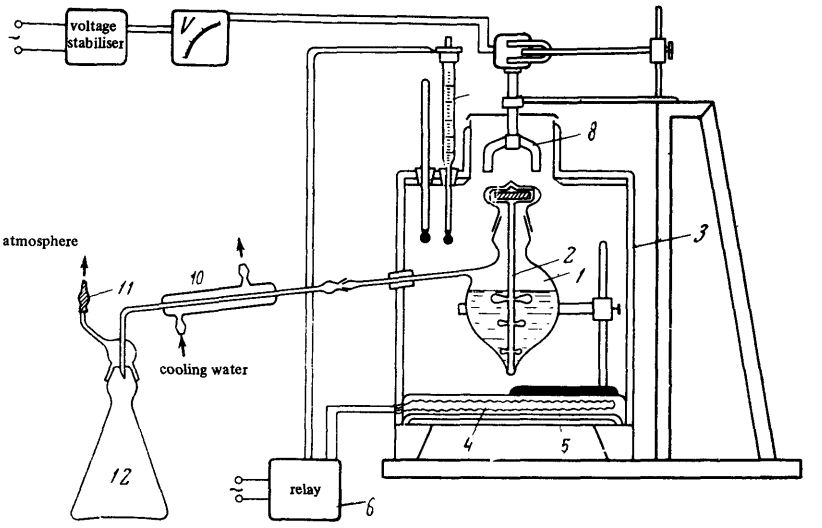

Figure 3. Apparatus for Rayleigh distillation; *1*) still; *2*) magnetic stirrer; *3*) air thermostat; *4*, *5*) electric heaters; *6*) relay; *7*) contact thermometer; *8*) magnet; *9*) voltage stabiliser; *10*) condenser; *11*) calcium chloride tube; *12*) receiver.

Here, V is the volume of the Rayleigh still, v_l is the molar volume of the liquid phase, v_V is the molar volume of the vapour phase, G is the number of moles of the mixture in the still, x and y are the mole fractions of the minority component in the liquid and the vapour phase respectively, z is the mean concentration of the minority component in G moles of mixture in the still; $x, y \ll 1$, $\alpha = y/x$, $\epsilon = \alpha - 1$.

As Fig. 4 shows, using the Rayleigh equation directly in the form (14a)–(14c) and (15a)–(15c) leads to large errors in the measurement of α, particularly at high degrees of condensation. If the separation is determined from an analysis of the vapour phase, and the degree of condensation is measured as the ratio G_0/G_i, the error is minimised, but even in this case degrees of condensation in excess of 10^2–10^3 lead to intolerably high errors in α.

7. Because of the need for visual observation of the progress of distillation and for an approximate estimate of the degree of condensation, evaporation stills are usually made of glass, which is not a good conductor of heat. This, in turn, produces significant temperature gradients at the walls of the still, and hence a temperature difference between the thermostat medium (air, or water) and the evaporation temperature must be specially maintained.

8. In addition to the designs involving mechanical stirring of the two phases, designs similar to the contact apparatus with rotating drums [7] and with inert carrier gas bubbling [31] have been proposed. These offer the advantage of a more precise temperature control of the contents of the still. In complicated systems, containing volatile impurities (see p. 574), this facility is extremely valuable, because the boiling point of these mixtures at constant pressure is a sensitive function of composition. Furthermore, the process takes place much faster, with a consequent reduction in the duration of the experiment. These designs can be additionally provided with facilities for liquid circulation, resulting in a large increase in the initial volume of liquid and hence in an enhanced ultimate degree of condensation and of separation. Lastly, these advanced designs allow the volume of vapour in equilibrium with the liquid to be kept small and constant, which largely removes the limitations discussed above and simplifies the experimental procedure.

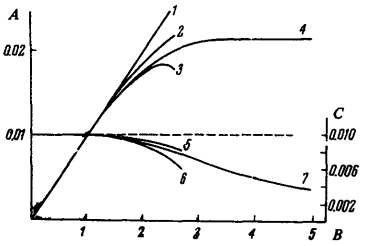

Figure 4. Plots of separation (x_i/x_f, x_i/z_f) against degree of condensation (G_i/G_f, g_i/g_f) assuming complete mixing of the vapour phase. Plots of the effective enrichment coefficient ϵ against degree of condensation assuming complete mixing of the vapour phase. *A*) values of $\lg\frac{x_i}{x_f}$ and $\lg\frac{x_i}{z_f}$; *B*) values of $\lg\frac{g_i}{g_f}$ and $\lg\frac{G_n}{G_f}$; *C*) effective ϵ values. Condensation conditions: initial amount of mixture $G_i = 10$ mole, volume of Rayleigh still $V = 0.6$ litre, molar volumes of liquid (v_l) and vapour (v_V) 0.05 and 22.4 litre mole^{-1} respectively, equilibrium value of the enrichment coefficient $\epsilon = 0.010$. Curves *1*, *2*, *3*, and *4* correspond to Eqns. (14a), (18a), and (18c) respectively. Effective ϵ values calculated from Eqn. (14a), allowing for the actual degrees of separation and condensation by means of Eqns. (18a)–(18b); curves *5*, *6*, and *7* correspond to Eqns. (18a), (18b), and (18c) respectively.

2. Rayleigh's Equation in a Form Suitable for Studying the Dependence of α on the Composition of the Phases

The integral forms of Rayleigh's equation given above were obtained on the assumption of constant separation coefficients α_{ik}. This condition is often inappropriate, and the equations given above then lead to some average value of α_{ik}. There is a simple method by which true values of α_{ik} can be obtained, and related to any concentration of the component k which is encountered during Rayleigh extraction [40,41]. A different mathematical procedure is used, based on a more convenient form [13] of the differential Rayleigh equation:

$$d\ln Q_{ik} = -\varepsilon_{ik}(d\ln G + d\ln x_k), \qquad (19)$$

whence

$$\varepsilon_{ik} = \frac{\dfrac{d\ln Q_{ik}}{d\ln G}}{1+\dfrac{d\ln x_k}{d\ln G}}. \qquad (20)$$

Since Q_{ik} varies as a function of G during the extraction, the wanted differentials are readily found from the analytical results obtained by any convenient method. The most accurate results are obtained by expressing $\ln Q_{ik}$ and $\ln x_k$ (or $\ln x_k$ and $\ln x_i$) in the form of Lagrange polynomials, which can then be differentiated numerically. Graphical differentiation procedures are also possible (from experimental plots of x against $\ln G$).

In the case of two-component mixtures the problem becomes simpler, since $x_2 = 1 - x_1$, and the relationship between $\ln x_1$ and $\ln G$ is sufficient to define α. For $\epsilon \ll 1$ (and particularly for $x_k \ll 1$) the differentials $\dfrac{d\ln x_k}{d\ln G}$ become negligibly small, and the expression takes the form

$$\varepsilon_{ik} = \frac{d\ln Q_{ik}}{d\ln G} = \frac{d\lg Q_{ik}}{d\lg G}. \qquad (21)$$

Examples of the use of these expressions can be found in the literature [29,40]. The experimental technique differs from the Rayleigh distillation procedure (see p. 577) in that the amount and composition of the distillate are monitored periodically. From these measurements it is a simple matter to calculate the amount and composition of the liquid in the still and to establish the dependence of $\lg Q$ upon $\lg G$. For the case of α = const this dependence will take the form, according to Eqn. (21), of a straight line of slope α.

3. Application of the Rayleigh Equation to Measurements of Separation Coefficients in the Presence of Additives, During Extraction, and During Ion Exchange

Additives showing preferential chemical or physical interaction with one or several of the components of a mixture, and therefore having a beneficial effect on the separation coefficient, have been used increasingly in recent years to facilitate the separation of difficult mixtures. Additives in various forms have been used in practically all countercurrent processes, in which separation depends on phase equilibria or chemical equilibria (azeotropic and extractive distillation, extraction and ion exchange at low degrees of complex formation in the aqueous phase).

The effective separation coefficient in the presence of additives is determined by two effects: the phase equilibrium, and the physical or chemical equilibrium between the initial forms of the components and the additive. The interaction can take place in one of the phases under study, or in both phases. In either case the Rayleigh process is complicated by the fact that the concentration of the additive (and therefore also α) varies as the condensed phase is removed. Nevertheless, useful analytical expressions for the separation coefficient relevant to the homogeneous exchange process can be obtained by making some specific assumptions as to the nature of the homogeneous exchange of the components between their initial form and their reaction products with the additive. This approach can be used to evaluate the effectiveness of the additive and to study the homogeneous reactions involving the additive.

Table 2.

Method	Logarithm of enrichment in the liquid phase as a function of degree of condensation. Isothermal regime	Logarithm of enrichment in the vapour phase as a function of degree of condensation. Isothermal regime
With involatile additive	$\ln\frac{z}{z_0} = \frac{1}{\alpha}\ln\frac{G_c+\beta G_a^0}{G_c+\beta G_a} - \ln\frac{G_c+G_a}{G_c+G_a^0}$	$\ln\frac{x}{x_0} = \frac{\alpha-1}{\alpha}\ln\frac{G_c+\beta G_a^0}{G_c+\beta G_a}$
With volatile additive	$\ln\frac{y}{y_0} = \frac{\gamma-\alpha}{\alpha(\gamma-1)}\ln\frac{\beta-c(\beta-1)}{\beta-c_0(\beta-1)} + \frac{(\alpha-1)\gamma}{\alpha(\gamma-1)}\ln\frac{c}{c_0}$	$\ln\frac{x}{x_0} = \frac{(\alpha-1)}{\alpha(\gamma-1)}\ln\frac{[\beta+(\gamma-\beta)\bar{c}]\bar{c}_0}{[\beta+(\gamma-\beta)\bar{c}_0]\bar{c}} + \ln\frac{\beta+(\alpha-\beta)\bar{c}}{\beta+(\alpha-\beta)\bar{c}_0}$
Extraction	$\ln\frac{Z_f}{Z_0} = \ln\frac{x_f}{x_0} = (\alpha-1)\frac{\delta R}{\alpha\delta R+S}\ln\frac{G_0}{G_f}$	
Ion exchange	$\ln\frac{x_f}{x_0} = \ln\frac{y_f}{y_0} = \frac{(\alpha-1)}{\alpha\delta R+S}\left[\delta R\ln\frac{G_S^f}{G_S^0} - \frac{S}{\alpha}\ln\frac{S+\alpha\delta R+(\delta-1)G_S^f}{S+\alpha\delta R+(\delta-1)G_S^0} - \left(\delta R-\frac{S}{\alpha}\right)\ln\frac{S+(\delta-1)G_S^f}{S+(\delta-1)G_S^0}\right]$	

G_S, G_R are the amounts of mixture in the system in the organic and the aqueous layer respectively;

R, S are the volumes of the organic and the aqueous phase in the case of extraction;

R, S are the molar capacities of the organic and the aqueous phase in the case of ion exchange.

The simplest case is found when the additive is present in the phase to be extracted and cannot be transferred to the phase to be removed [35]. Such a process is characterised by the phase separation coefficient α and also by a separation coefficient β which relates to the homogeneous reaction in the phase to be extracted. Then, from the differential form of the Rayleigh equation, we obtain

$$\frac{dz}{z-x} = \frac{dG}{G},$$

where z is the mean concentration of the given component, G is the amount of mixture in the phase to be extracted, and x is the concentration of the same component in the phase to be removed. Starting from the differential form of the Rayleigh equation we can arrive at a number of expressions for isothermal conditions: these are set out in Table 2. They all involve the assumption that the phase and the homogeneous exchange equilibria are maintained at all times. Very low concentrations of the particular component are also assumed (x, $z \ll 1$).

The case of an additive which can distribute itself between the two phases is more complicated [36]. On the

assumption that equilibrium in the phase to be removed is determined by the same coefficient (β) as in the phase to be extracted, and that the distribution of the additive between the two phases can be described in terms of a distribution coefficient γ, the integral forms of Table 2 can be obtained from the differential form. Analogous expressions can be derived for the isobaric regime, but these are complicated by the need to allow for the temperature dependence of α.[35]

In the above discussion of non-distributed and of distributed additives, the volume of phase to be removed (in equilibrium with the phase to be extracted) is assumed to be negligibly small. This condition is easily satisfied in Rayleigh distillation, but not in extraction or in ion exchange processes. In the latter, the condition of constant volume of the two contacting phases is more easily realised. Hence, and using the distribution coefficient δ to characterise the phase equilibrium of the mixture as a whole for extraction systems and δ' for ion exchange systems, appropriate integral forms of the Rayleigh equations can be obtained[37]. These, too, are given in Table 2.

The tabulated relationships are transcendental in α and β (with the exception of the extraction equation). Hence, the required values must be found by selection or by successive approximation methods, which are in general very time-consuming.

VI. SQUARE CASCADE METHODS

The term square cascades is used[42] in the general theory of separation processes to denote columns operating in the countercurrent regime and characterised by a constant flow of material at any cross-section. We shall retain this term in order to include in the following discussion, without distinction of any kind, processes such as rectification, extraction, hypersorption, development chromatography, heterogeneous isotope exchange, and others. Cascade methods enable the separation effects under study to be strongly enhanced, leading to reliable and accurate measurements of α and ϵ. It is usually necessary to resort to these methods when ϵ is small, particularly if the apparatus is simple and no preliminary investigation of the process is required (rectification, development chromatography).

The separation obtainable in square cascades is characterised by the number of theoretical plates (n), which is a function of the hydrodynamic operating regime of the cascade, and of the properties of the mixture to be separated. Thus, the determination of α by a cascade method is always a problem with two unknowns, requiring two independent equations. Bearing in mind that the measurement error associated with various characteristics of the process can seriously degrade the accuracy of the measurement of α and n, it is often the best practice to extract these values from the largest possible number of experiments over the widest possible range of cascade parameters.

1. Equations for Stationary Operating Regimes of the Cascade

States of the cascade for which all parameters and their characteristics remain constant with time are termed stationary states.

We shall deal first with the equations and methods which apply to total reflux conditions. The separation Q_{ie} is related to the separation coefficient α_{ie} of a cascade with n theoretical stages by the Fenske-Underwood equation[43,44]

$$Q_{ie} = \alpha_{ie}^{n}. \qquad (22)$$

In order to calculate α_{ie} from the experimentally observed value of Q_{ie} we must know the number n of theoretical separation stages under the conditions of the particular experiment. In the case of two-component mixtures, we can use the mass conservation equation for one of the components for this purpose, and arrive[45] at the following analytical expression for α:

$$\ln \alpha = \frac{G \int_{h_1}^{h_2} (x - x_0)\, dn}{G \cdot \ln \frac{1 - x_{h_2}}{1 - x_{h_1}}}.$$

In this expression the numerator is the experimentally measurable excess of the component under study in a section of the cascade between points h_1 and h_2 (as compared with the initial state, for which the concentration is everywhere x_0). G is the number of moles of material in the same section of the cascade, x_{h_1} and x_{h_2} are the concentrations of the component at the points h_1 and h_2.

In practice, measurements of α have often been made by inserting into the Fenske–Underwood equation the number of theoretical plates, obtained by independent methods. The precision of the measurement of α by Fenske–Underwood equation is much more sensitive to errors in n than to errors in Q_{ie}:

$$\frac{\Delta \ln \alpha_{ie}}{\ln \alpha_{ie}} = |\Delta \ln \ln Q_{ie}| + |\Delta \ln n|. \qquad (23)$$

For the case of rectification in unpacked, liquid-film columns the number of plates n can be calculated to an accuracy of 10–15% from the parameters of the column and from the flow by using semi-empirical relations[46,47]. This calculation cannot yet be made in the case of the more efficient, packed columns, and an approximate estimate of α for these columns is sometimes made by inserting the value of n obtained for a model mixture (with physicochemical properties as close as possible to those of the unknown mixture) in the same cascade[45]. Bushmakin and coworkers[48–50] suggested the measurement of α at low concentrations of one of the components by using the number of theoretical plates (n) obtained in experiments with the same mixture but at concentrations high enough to allow α to be measured by other methods. This procedure ignores the dependence of the HETP (height of the equivalent theoretical plate) upon composition, and must therefore be treated as approximate.

More accurate values of α are obtained if the separation Q and the number of plates n can be measured in a single experiment. This condition can be realised if the unknown mixture contains more than two components, and the separation coefficient α_{ik} for one pair of components is known. In this case there is a simple relationship which allows the unknown separation coefficients to be evaluated in terms of the known value α_{ik}:[51,52]

$$\ln \alpha_{em} = \ln \alpha_{ik} \frac{\ln Q_{em}}{\ln Q_{ik}}. \qquad (24)$$

The equations for stationary separation regimes of multicomponent mixtures with take-off are complicated, and cannot be applied to the measurement of α. The numerous and simpler relationships which have been proposed for binary mixtures[53–59], on the other hand, can be used. Experimental tests of some of these equations have been carried out[60–62]. The procedure for measuring α in

the presence of take-off involves measuring the separation of the mixture by the cascade either as a function of relative take-off or as a function of the position of the take-off point (multipoint take-off). In both cases a large number of experiments is desirable, followed by statistical treatment of the results, because the separation is very sensitive to the take-off ratio, which cannot be measured with great precision. Since the equations for the take-off regime are transcendental in α, it is convenient to use the so-called graphical least-squares method, which does not require normal equations to be set up[63,64]. Smoker's equation, which applies for any value of α and any concentration of either component, is presented in Table 3.

Table 3. Operating equation of the column in the stationary regime:

$$\left(\frac{\alpha}{\gamma c^2}\right)^n = \frac{x'}{x}\left[\frac{1-\left(\frac{\gamma c(\alpha-1)}{\alpha-\gamma c^2}\right)x}{1-\left(\frac{\gamma c(\alpha-1)}{\alpha-\gamma c^2}\right)x'}\right]. \qquad (25)$$

Variable	Section of cascade	
	Rectifying	Scrubbing
x'	$x_p-\beta$	$x_0-\beta$
x	$x_0-\beta$	$x_p-\beta$
c	$1+(\alpha-1)\beta$	
β root of equation $(0\leq\bar{x}\leq 1)$ $0<\beta<1$	$\gamma(\alpha-1)\bar{x}^2+[\gamma+b(\alpha-1)-\alpha]\bar{x}+b=0$	
b	$x_p\Theta$	$-\frac{x_p\Theta}{1-\Theta}$
γ	$1-\Theta$	$\frac{1}{1-\Theta}$

γ is the ratio of heavy phase and light phase flows; Θ is the relative take—off (product/feed); x is the reduced concentration in the heavy phase; subscripts 0 and p refer to the feed and the outlet section respectively.

Simpler equations, shown in Table 4, are used for the low-concentration region, when the equilibrium equation is linear[45,65-67].

2. Expressions for Non-stationary Regimes

During the establishment of a stationary state at any point in the cascade, the concentrations of the components show a continuous change which is (to a first approximation) exponential. In principle, the separation coefficient of a binary mixture can be calculated from measurements of the concentration of one of the components as a function of time. However, none of the many expressions which have been proposed to describe the achievement of steady state is truly exact[45,65,67-75]. This is because of the lack of accurate methods of solution of non-linear partial differential equations, such as the basic non-stationary state equation. The equations which have been proposed involve various simplifying assumptions on the distribution of concentrations along the column and with time; these assumptions do not usually lend themselves to strict mathematical analysis, and existing experimental data are insufficient for a detailed study of the assumptions.

The adequacy of the equations for non-stationary processes is most satisfactorily established by comparing the numerical values of various parameters given by the equations with the values obtained by numerical solution of the original differential equation on an electronic computer. Jackson and Pigford (quoted in Ref. 72) were able to show in this way that some published equations[68,70,71] were unacceptable. Other equations[72,74] were shown to be inaccurate by comparison with experimental results[45,67].

Table 4. Operating equations of the column in the stationary regime for the case $x \ll 1$.

Section	Component	
	light	heavy
Rectifying	$Q=\frac{x_p}{y_0}=\frac{(\alpha-\gamma)\left(\frac{\alpha}{\gamma}\right)^n}{\gamma(\alpha-1)+\alpha(1-\gamma)\left(\frac{\alpha}{\gamma}\right)^n}$	$Q=\frac{y_0}{x_p}=\frac{\gamma(\alpha-1)(\alpha\gamma)^n-(1-\gamma)}{(\alpha\gamma-1)}$
Scrubbing	$Q=\frac{x_0}{x_p}=\frac{\left(\frac{\alpha}{\gamma}\right)^n(\alpha-1)-(\gamma-1)}{(\alpha-\gamma)}$	$Q=\frac{x_p}{x_0}=\frac{(\alpha\gamma)^n(\alpha\gamma-1)}{(\alpha-1)+\alpha(\gamma-1)(\alpha\gamma)^n}$

γ is the ratio of heavy phase and light phase flows; n is the number of theoretical plates; x is the concentration in the heavy phase; y is the concentration in the light phase; subscripts 0 and p refer to the feed and the outlet ends of the section respectively.

The equation of Babkov and Zhavoronkov[75] was tested most stringently against experiment and against a model of the achievement of steady state (electronic computer), and the discrepancy during the relaxation time was found to be insignificant (0.6%). Rozen's equation[67] also gave satisfactory results. The full forms of these equations are shown in Table 5 together with approximate expressions applicable at low concentrations. All these equations are transcendental in α and Q_∞ (degree of separation at steady state). The usual procedure for calculating α is to insert the rather inaccurate experimental values of Q_∞ into the kinetic equations. An additional source of error could be the inaccuracy of the kinetic equations themselves at times long compared with the relaxation time. The most satisfactory procedure is to calculate α and Q_∞ together by least squares[63].

The mass conservation equation for either of the components to be separated can be used as an additional source of information on the value of α. When high-efficiency cascade processes are used, the kinetic curves show an extensive linear portion, indicating that during an appreciable time the longitudinal transfer of any component is practically constant and is determined by the difference in equilibrium concentrations at the feed plate of the cascade. If the cascade flows (L) are constant, measurement of the amount of component i accumulating in the cascade in time t ($G\int_0^n (x_i - x_{i_0})dn$) enables this difference to be determined.

$$y_i^0 - x_i^0 = \frac{G\int_0^a (x_i - x_i^0)\,dn}{tL} \qquad (26)$$

The equations relating this difference to α_i can then be used to evaluate the latter.

Unlike the kinetic methods described above, the mass balance method offers two important advantages: on the linear portion of the kinetic curve, Eqn. (26) is both accurate and applicable to multicomponent systems. Of course, with multicomponent systems it becomes necessary to measure the integrated transport of all the components, whether or not the experimenter is interested in their separation. The accuracy of measurements of ϵ by this method is well illustrated by the excellent agreement with results obtained by other methods [67,76].

Table 5.

Region of application	Analytical expressions for the time to reach steady state	Literature references
$0<x\leqslant 1$	$t=\frac{1}{L}\left\{\frac{\varepsilon}{1+x_0\varepsilon}+\frac{\alpha}{\varepsilon(1-x_0)(1+x_0\varepsilon)^2}\left[(\alpha^n-1)\frac{1-x_n}{x_n-x_0}+\varepsilon\right]\ln\left(1+\right.\right.$ $\left.\left.+\frac{1+x_0\varepsilon}{x_0(\alpha^n-1)\frac{1-x_n}{x_n-x_0}}\right)\right\}\times\left[(x_n-x_0)\left(v_0-\frac{Hn}{\frac{1-x_n}{1-x_0}\alpha^n-1}\right)+\right.$ $\left.+\frac{H(\alpha^n-1)}{\ln\alpha}\cdot\frac{\frac{1-x_n}{1-x_n\alpha^n-1}}{1-x_0}\cdot\ln\frac{1-x_0}{1-x_n}\right]$	75
$x\ll 1$	$t=\frac{1}{L}\cdot\frac{\alpha}{\alpha-1}\left[\left(H\frac{\alpha}{\alpha-1}+v_0\right)\cdot(\alpha^n-1)-nH\right]\cdot\ln\frac{\alpha^n-1}{\alpha^n-\frac{x_n}{x_0}}$	75
$0<x\leqslant 1$	$M=\left\{v_0\frac{(\alpha^n-1)(1-x_0)}{1+x_0(\alpha^n-1)}+H\left[\frac{\ln[1+x_0(\alpha^n-1)]}{x_0\cdot n\cdot\ln\alpha}-1\right]\right\}x_0;\ t_0=\frac{M}{j_0}$	67
$x\ll 1$	$t_0=\frac{\left[v_0(1-e^{\varepsilon.i})+H\left(1-\frac{1-e^{\varepsilon.i}}{\varepsilon n}\right)\right]}{L\varepsilon}$	67

t is the time to reach steady state, L is the flow of material in the column (mole h^{-1}), x_0 and x_n are the initial and the final concentration, n is the number of theoretical plates, H is the delay for one plate, v_0 is the capacity of the still, t_0 is the total relaxation time of the column, j_0 is the limiting transfer, M is the total equilibrium hold-up in the column.

VII. CHROMATOGRAPHIC METHODS

The field of application of chromatographic methods of measuring separation coefficients is rapidly expanding. It already includes phenomena such as liquid–vapour and liquid–gas equilibria, sorption of vapours and gases on solid sorbents, ion exchange and non-ionic sorption on resins, liquid–liquid equilibria, and homogeneous reactions in solutions. These methods are being applied to the separation of a wide variety of mixtures. Examples of their successful application to the separation of every kind of difficult mixture can be found in numerous textbooks, review articles, and bibliographies. We need only mention some of the most important classes of mixtures: isotopes, isomers, inorganic and organic polymers, rare earths and actinides, numerous homologues and genetically related compounds, aminoacids, polypeptides, sugars, and other biologically active materials.

All three main variants of the chromatographic process (elution, frontal, and displacement methods) can be used to measure small separation coefficients. The development or elution method has attracted most attention, the frontal method has attracted the least. A vast amount of work has been devoted to the separation of the most diverse materials by elution, but often the authors have neglected to calculate the separation coefficients even when sufficient information was available.

We shall consider below the special equations which allow measurement of ϵ from quite small separation effects in small columns. These equations are valuable mainly in measurements of $\epsilon \ll 1$, i.e. in problems as difficult as isotope separation, but they can also be used successfully in the study of many other difficult mixtures.

1. Elution Chromatography

The principle of the method is the following: a sample of the mixture to be separated, containing much less material than the total capacity of the sorbent in the column, is introduced at the top of the chromatographic column. A mobile phase (liquid or gas) containing a displacement agent is then used to elute the sample. The condition for the establishment of the elution regime is that the affinity of the displacement agent for the sorbent must be less than the affinity of any component of the mixture. As a result of elution, the components move downwards along the column, at different rates, and gradually become separated. In addition, each individual band becomes broader as it moves downwards. The effluent at the bottom of the column consists of concentration waves of the various components, overlapping to a greater or lesser extent. The extent of overlap depends on the distribution coefficients of the components between the mobile and the stationary phase, and also on the length and the efficiency of the packing, and on the operating regime of the column. Initially, the form of the concentration peaks depends on the type of the adsorption isotherms of the components, but further down the column it approaches the shape of a Gaussian distribution. If the adsorption isotherms are linear and mutually independent, the relationship between the distribution coefficients λ_i of the components, their separation coefficients α_i, and the volumes v_i and v_j of the mobile phase for which the respective concentrations are at a maximum takes the simple form

$$\alpha_{ij}=\frac{\lambda_i}{\lambda_j}=\frac{\bar{v}_i-v_0}{\bar{v}_j-v_0};\quad \varepsilon_{ij}=\frac{\bar{v}_i-\bar{v}_j}{v_j-v_0}, \tag{27}$$

where v_0 is the free volume of the column.

Thus, the measurement of separation coefficients by elution chromatography involves, firstly, the establishment of conditions consistent with the assumptions made in the derivation of the equations, and secondly a very accurate measurement of the quantities $\bar{v}_i$, $\bar{v}_j$, and v_0.

The condition of linearity and mutual independence of the sorption isotherms is best satisfied at low concentrations of the materials to be separated. However, the initial concentration of the mixture in the mobile phase is usually fairly large, and in relatively short columns the concentration peaks do not achieve the Gaussian form. In long columns, the concentration peaks travel through most of the distance at fairly low concentrations, such that the sorption–desorption process takes place in the linear part of the isotherm. Also, the components in this case are almost completely separated provided that the enrichment coefficient ϵ is not too small, and the problem of possible interaction between the components ceases to be relevant. If the separation achieved is sufficient to allow direct measurement of $\bar{v}_i$ and $\bar{v}_j$, the separation coefficient is measured directly by means of Eqn. (27).

When the isotherms show substantial deviation from linearity, the concentration peaks are often seriously distorted when separation is complete. In these cases formula (27) gives only approximate values of ϵ_{ij}, and a better estimate is obtained by inserting $\bar{v}_i$ values corresponding to the centre of gravity of the various bands [77] instead of the concentration maxima.

When $\epsilon_{ij} \ll 1$, and also when short columns are used, the individual bands overlap so strongly that direct determination of $\bar{v}_i - \bar{v}_j$ is impossible: the detector finds only a combined peak for two or more components, and its shape is indistinguishable from that of the individual components. Special relationships, allowing indirect measurement of $\bar{v}_i$ and $\bar{v}_j$, must then be used.

By applying the general theory of elution chromatography [78] to the separation of substances with closely similar properties, Glueckauf obtained [79] the following relationship between the separation of the components i and j and the elution volume v:

$$\ln Q_{ij} = \varepsilon_{ij} N \frac{\bar{v}_\Sigma - v}{\sqrt{\bar{v}_\Sigma - v}}, \qquad (28)$$

where $\bar{v}_\Sigma$ is the elution volume corresponding to maximum total concentration and N is the number of theoretical plates in the column†. Glueckauf's expression can easily be converted into the form

$$\varepsilon_{ij} = -N \frac{d \ln Q_{ij}}{d \ln v}. \qquad (29)$$

The precision with which ϵ can be measured depends on the precision of the estimate of N as well as on the precision of the measurement of separation as a function of volume. When the shape of the elution waves corresponds accurately to the normal Gaussian distribution the value of N can be calculated [77] by the expression

$$N = 8\left(\frac{\bar{v}_\Sigma}{B}\right)^2, \qquad (28a)$$

where B is the width of the peak at a concentration a factor of e below the maximum. If the peak is distorted, on the other hand, it is better to use Keuleman's expression

$$N = 16\left(\frac{\bar{v}_\Sigma}{W}\right)^2, \qquad (28b)$$

where W is the base of the triangle obtained by drawing two tangents through the points of inflection of the elution peak.

Two unsatisfactory aspects of Eqns. (28) and (29) must be pointed out. Firstly, the calculation of ϵ requires a knowledge of the differential of the degree of separation with respect to volume, involving at least ten measurements of Q_{ij} for different fractions of the total peak. Secondly, these equations assume relatively large column lengths, in which the total capacity of the sorbent is large compared with the amount of material in the initial sample. Some expressions compatible with simpler experimental procedures are described below.

As before, we assume [82] that the individual peaks are in every way similar to the combined peak, i.e. we consider only very weak separations of the peaks. No assumption is made as to the shape of the peaks, and therefore no limitation is imposed on the size of sample in relation to the capacity of the column. According to this method, the concentration peak at the outlet of the column is divided into two parts containing approximately equal amounts of the mixture. These two parts are then analysed for the components. Consider the separation of a binary mixture. The general expression takes the form

$$\Delta x = x_t - x_h = \frac{(m_h + m_t) \cdot \varkappa_0 c_\Sigma \varepsilon (\bar{v}_\Sigma - v_0)}{\{m_t (1+\varkappa_0) + c_\Sigma \varepsilon [N - \varkappa_0 (1-N)] (\bar{v}_\Sigma - v_0)\}} \times \times \frac{1}{\{m_h(1+\varkappa_0) - c_\Sigma \varepsilon [N - \varkappa_0 (1-N)] (\bar{v}_\Sigma - v_0)\}}, \qquad (30)$$

where x_t and x_h are the mole fractions of the component in the tail and the head parts of the combined peak, m_t and m_g are the amounts of mixture in the same parts, c_Σ is the total concentration at the point where the peak is cut, $\kappa_0 = x_0/(1 - x_0)$, $\bar{v}_\Sigma$ is the elution volume corresponding to the centre of gravity of the combined peak, v_0 is the free volume of the column, N is the tail section of the base of the triangle W (see above) defined by the tangents to the peak.

For $m_t \simeq m_h$ the expression simplifies to

$$\varepsilon = \frac{(1+\varkappa_0)^2 \cdot \Delta x (m_t + m_h)}{4 c_\Sigma \cdot \varkappa_0 \cdot (\bar{v}_\Sigma - v_0)}. \qquad (31)$$

Eqn. (30) can be generalised for the case of a multicomponent mixture, involving division of the peak into several parts [83].

2. Development and Frontal Chromatography Method

In the development chromatography method, the mixture to be separated moves along the column in the form of steady-state bands which retain their linear dimensions by virtue of a specially chosen set of conditions (initial form of the sorbent, presence of a desorbent). In a system of coordinates strictly related to the steady-state band, this method has the properties of a rectangular cascade operating in the total reflux regime [76,84]. Hence, all the expressions derived for the evaluation of α and ϵ in rectangular cascades are applicable in principle to the development chromatography method. The total reflux [84] and constant transfer [76] methods have been used in practice.

Separation by the frontal method is also described by rectangular cascade equations. The only difference from the development variant is that the band of varying concentrations (or band of concentration gradients) must now be treated as a rectangular cascade operating in the open mode [67,85].

VIII. CRAIG'S METHOD (COUNTERCURRENT EXTRACTION)

The principle of the method is as follows [86]. We postulate a system containing a sufficiently large number of identical contact cells in series, which can be interconnected at will, and containing equal amounts of phase A. At time zero, we introduce into the first cell a volume of the second phase (B) containing two substances I and II, whose exchange with phase A involves linear distribution isotherms:

$$\frac{c_{IA}}{c_{IB}} = \lambda_1 \text{ and } \frac{c_{IIA}}{c_{IIB}} = \lambda_2.$$

After sufficient time, equilibrium distribution of the two substances between the phases will be established in the first contact cell. The mobile phase B is then completely transferred to cell 2, and the same volume of phase B

†An expression similar to Glueckauf's has been proposed independently [80]. However, the authors (who used the Mayer–Tompkins theory of chromatography [81]) treated elution as a stepwise process, and therefore their expression is inaccurate.

(without the substances to be separated) is introduced into cell 1. Equilibrium is again allowed to develop in both cells, and the equilibrium phase B is transferred from cell 1 to cell 2 and from cell 2 to cell 3, pure phase B being again added to cell 1. All these operations are then repeated the requisite number of times. The overall operation shows some close similarities to elution chromatography, from which it differs only in that the equilibration processes and the relative motion of the phases are separated in time, and the motion of the two phases is stepwise.

However, these differences are reflected only in the quantitative aspects of the problem. The distribution curves of the components after a sufficiently large number of steps look like elution chromatograms, and correspond to the normal Gaussian distribution. In common with elution chromatography, the method allows any number of components to be separated at the same time (Fig. 5). Furthermore, the Craig method is a more complex variant of the multistage condensation method, since the tail fractions of both phases are effectively subjected to multistage stripping, and their compositions must therefore obey the equations which describe this method.

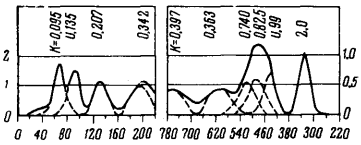

Figure 5. Distribution of aminoacids in a 220-cell Craig apparatus. From left to right, peaks correspond to tryptophan, phenylalanine, leucine, isoleucine, tyrosine, methionine, valine, α-aminobutyric acid, alanine, and glycine.

The theory of elution chromatography with stepwise motion of the mobile phase developed by Mayer and Tompkins [81] is fully applicable to the Craig process. This theory gives the relationship between the coefficients of the isotherms of the components, the ordinal number (p) of the volume of mobile phase, the ordinal number (n) of the contact cell, and the concentrations of the components in either phase.

Three methods of determining small separation coefficients in systems equipped with a sufficient number of contact cells can be distinguished.

1. By analogy with the elution chromatography method, we can use Eqn. (26), allowing however for the fact that $v_0 = 0$. According to Mayer and Tompkins [81], the maximum concentration of any component is achieved, for a given number n of cells, after the passage of a volume $P_i = n\lambda$. The maximum values of c_i and c_j are related by

$$\varepsilon_{ij} = \frac{\overline{P}_i - \overline{P}_j}{\overline{P}_i}.$$

If ϵ_{ij} is large enough, P_i and P_j can be determined directly by any convenient analytical method, and a large number of contact cells is no longer required. But if $\epsilon_{ij} \ll 1$, it becomes possible to measure ϵ indirectly (as in Glueckauf's method). The concentrations of components i and j in the fractions of the mobile phase appearing at the outlet of the Craig system are related by the equation (in which n = const)

$$\ln \frac{c_{ip}}{c_{jp}} = \ln \frac{\lambda_1}{\lambda_2}(p-1) + (p+n)\ln \frac{1+\lambda_2}{1+\lambda_1}. \quad (32)$$

After differentiation and some simplification we arrive at the expression

$$\ln \alpha = \frac{d \ln Q_{ij}\,(1+\lambda)}{dp}, \quad (33)$$

where λ is the distribution coefficient for the combined substances i and j.

2. If the Craig process is carried out with $p \leq n$ (i.e. no mobile phase is withdrawn at the outlet of the system), it is easy to show by means of the Mayer–Tompkins theory that the separation of the components in the two extreme cells (numbers 1 and n) are described by Eqn. (34). In this variant, the equality

$$p + n = p' + 1,$$

applies in any cell, where p' is the total number of steps made in the system. Substituting this equality into Eqn. (32) we arrive at [76]

$$\ln Q_{ij} = (n-1)\ln \alpha; \quad \alpha = \frac{d \ln Q_{ij}}{dn}. \quad (34)$$

3. Lastly, as stated above, the end fractions of both phases undergo double multistage extraction in Craig's process, and therefore any of the expressions given above for the multistage condensation method can be used to calculate the separation of the components in the end fractions. In one sense, the Craig process is more economical (by a factor of two) than the normal double multistage condensation method. Half as many operations are needed to achieve a given separation, since one Craig operation results in the extraction of both end fractions.

The process has so far been applied only to the separation of substances by extraction, because the two phases can be separated rapidly and quantitatively with the apparatus developed by Craig and Past [87]. In principle, however, the method is applicable to any system including a mobile liquid phase, i.e. to the whole range of solution–sorbent systems. The main use of the method has been as a convenient laboratory means of separating substances and analysing mixtures.

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Mendeleev Moscow Chemical
Engineering Institute

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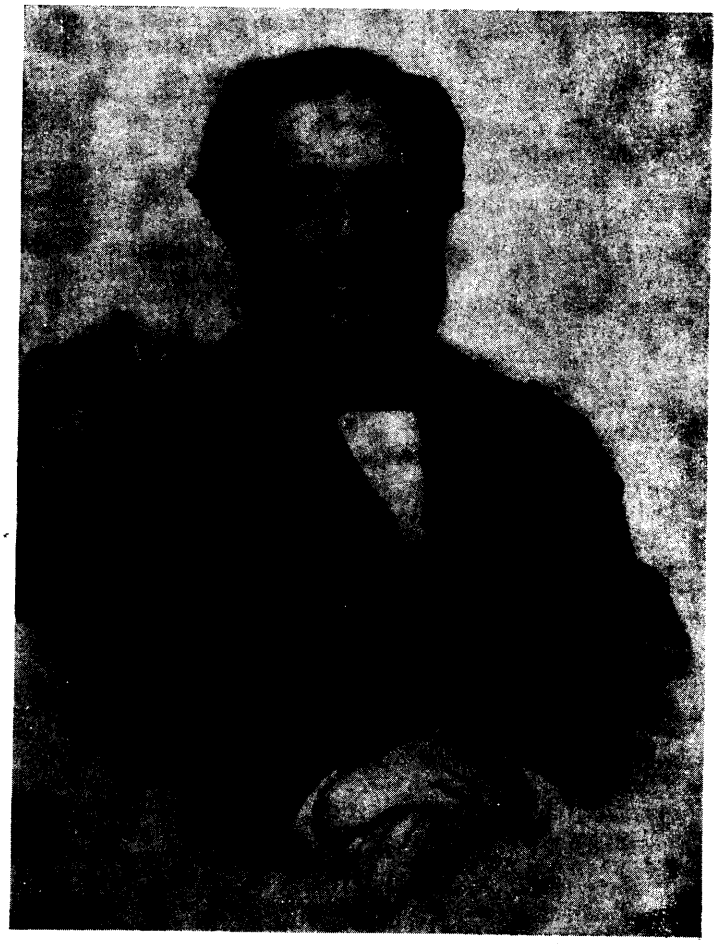

D.I.Mendeleev in 1869.

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D.I.Mendeleev and His Discovery

V.N.Kondrat'ev

The centenary of D. I. Mendeleev's discovery of the Periodic Law of the chemical elements is being celebrated during 1969 by scientists in many parts of the world. The significance of this discovery in relation to the development of chemistry, physics and borderline sciences as well as for the advancement of agriculture and industry cannot be overestimated. It is impossible to visualise modern science and technology without the Periodic Law which has been a guide line both for theoretical and practical advances.

Mendeleev's discovery of the Periodic Law was not an accident. He, like many scientists whose names are associated with some scientific discovery, had predecessors. The discovery of the Periodic Law is a particularly good example of the sequential type of scientific thinking which is characteristic of all sciences and of all periods in time.

In order to understand the position which chemistry had reached by the time the Periodic Law was discovered one must recall the great chemical revolution associated with Lavoisier, the celebrated French scientist. In Lavoisier's time chemistry consisted of a mass of facts which needed to be arranged systematically and comprehended. Lavoisier created a new system in chemistry by drawing on the experience of his predecessors and his contemporaries and on the results of his own experiments; this system completely refuted the then accepted phlogiston theory. In his "Elementary Course of Chemistry" written in 1789, Lavoisier gives a list of "simple substances" which formed the foundation of the chemical nomenclature which he introduced. Among these simple substances Lavoisier distinguished what he termed "elements", defining them as simple substances which could not be broken down by chemical analysis. He included among them oxygen, nitrogen and hydrogen which he had discovered. Lavoisier was clearly aware of the fact that the concept of "a simple substance—an element" which he had introduced was in a sense relative, since, as he said in his text-book of chemistry "a given substance represents the contemporary limit of chemical analysis" since "at the present stage of our knowledge, analysis cannot further fragment it".

In fact all the subsequent advances in analytical chemistry, which had been enriched by new techniques (to mention a few; gas analysis, electrolysis, spectroscopic analysis), have characteristically led to the separation of a number of Lavoisier's simple substances into elements which could not be broken down any further. Many new elements were already discovered in the first quarter of the nineteenth century. Among the alkali metals discovered then were lithium, sodium and potassium, among the halogens—fluorine, chlorine and iodine; a series of metals of the platinum group—palladium, rhodium, osmium, iridium and ruthenium (platinum itself having been discovered in the eighteenth century), a number of alkali and alkaline earth elements, and many other elements were discovered at the beginning of the nineteenth century. Their discovery is associated with the names of such renowned scientists as Berzelius, Gay-Lussac, Davy and many others—chemists and physicists from many countries: Britain, France, Germany, Holland, Sweden, Russia and others.

The large numbers of elements newly discovered now had to be designated. The symbols for the elements which have been retained to the present day were proposed by Berzelius in 1813.

Dalton's atomic theory (1803), published by him in 1808 in a two-volume book "A New System of Chemical Philosophy", played a key role in defining the concept of an element. One of the hypotheses of Dalton's theory states that "every chemical element consists of simple atoms proper to it, which are different from the atoms of every other element". With the help of symbols which he introduced, Dalton could represent the molecules of various compounds (he called molecules complex atoms) by formulae which were sometimes quantitative. Thus, for example, he represented the molecule of carbon dioxide by a formula which consisted of three spheres—two white ones (representing atoms of oxygen) on the outside and a black one (representing an atom of carbon) between them. These were the first quantitative chemical formulae.

The discovery of new elements was parallelled by investigations of the chemical and physical properties of the elements and their compounds. In order to determine the structure of various substances it was essential to know their elemental composition quantitatively. Bergman in Sweden was the first to begin quantitative study of the composition of chemical substances, he started as early as 1770. Lavoisier placed exceptional emphasis on the quantitative analysis of substances and he, together with the French school of chemists and chemists in other countries, were responsible for developing many new techniques for exact quantitative analysis. The quantitative study of chemical substances is based on the law of the constancy of their composition. The French chemist Proust, who was much concerned with the preparation of chemically pure substances and their analysis, formulated this hypothesis as follows: "Nature, even through the agency of man, never produces compounds without scales in her hands—by weight and by measure". The techniques of quantitative analysis naturally continued to improve with time, reaching ever greater degrees of precision.

Much attention was paid to the study of the chemical properties of the elements. Investigations of the composition of chemical substances led to the concept that all substances were formed by the substitution of some atoms or groups of atoms by other ones. This view was first expressed by Dumas and Regnault in 1840 and developed further by Gerhardt and Kekulé. It followed from this concept that the atom of each element has a certain "capacity", i.e. can substitute or add on only a quite definite number of other atoms. This conclusion was reached by the British chemist Frankland in 1848-1852. The quantitative measure of such capacity is given by the valency of the atom—a term introduced by Wichelhaus in 1868.

Long before this, at the end of the eighteenth and beginning of the nineteenth century it was shown that chemical elements combined with one another in definite ratios by weight, which in itself asserted the constant nature of chemical substances. Analysis of oxygen compounds resulted in determining the amounts of various elements which combined with the same amount of oxygen. Wollaston (1814) called these values chemical equivalents. Ber-

zelius and Richter were largely responsible for determining precisely the weight ratios and chemical equivalents of elements. Faraday, working on the quantitative studies of electrolytic phenomena, opened up new possibilities for measuring chemical equivalents. Faraday measured the amounts of various elements by passing the same current through a solution of electrolyte and referring these to the amount of one of the elements, calling them electrochemical equivalents. The latter proved to be identical with the chemical equivalents. When the concept of valency was introduced it became evident that these values represented the ratio of the atomic weight to the valency of an element.

Thanks to the accuracy of determining the weight ratios of the elements Berzelius could determine equally precisely the atomic weights of many of the elements known in his day. The Belgian chemist Stas should be mentioned here; he determined very accurately the atomic weights of oxygen, silver, nitrogen, sulphur, chlorine, bromine, iodine, potassium, sodium, lithium, lead and carbon using his measurements of chemical equivalents. The Avogadro hypothesis played an important part in the exact determination of gaseous substances. Taking this hypothesis as a basis, Cannizzaro proceeded in the eighteen-fifties to establish more precisely the atomic weights of a series of elements, including hydrogen, oxygen, chlorine and others. Dulong and Petit found in 1819 that the product of the heat capacity of a solid element and its atomic weight had a constant value (the Dulong and Petit Law). Using this Law, Regnault first found the correct atomic weights of bismuth, silver, potassium and sodium, and Cannizzaro determined the atomic weight of copper and other elements.

As the result of the Herculean labours of many chemists and physicists from various countries and nations by 1869 there were 64 elements instead of the 35 simple substances of Lavoisier (1789), of which no more than 20 could be accurately described as elements; for most of these 64 elements the atomic weights were known sufficiently accurately, as were their chemical and some physical properties. All this accummulated material now needed to be systematically arranged.

The first attempt in this direction was made by Doebereiner who as early as 1829 noted that some elements which were similar in their chemical properties could be grouped into threes (triads). Such triads included: chlorine, bromine and iodine; lithium, sodium and potassium; and calcium, strontium and barium. At the same time in each such triad there was some consistency in relation to the atomic weights of the elements forming the given triad, viz., the atomic weight of the middle element in the triad was approximately equal to the arithmetic mean of the atomic weights of the two end elements. In 1851 Dumas gave some attention to Doebereiner's triads.

In 1850 Pettenkofer published a table of the equivalent weights of eighteen elements, arranged in five groups consisting of elements with similar chemical properties. Three of these groups included the elements which figured in Doebereiner's triads, but they now consisted of four elements, e.g. oxygen, sulphur, selenium and tellurium formed a group. He also noted that the difference of the equivalent weights in each group was approximately a multiple of a whole number. In the lithium, magnesium and oxygen groups this number equalled 8. Analogous groups of elements also appeared in Dumas (1851). In 1857 Lenssen's table appeared, in which he quite formally grouped all the elements then known into triads, with the result that some triads contained as chemically dissimilar elements as, for example, oxygen, nitrogen and carbon. In 1862 de Chancourtois arranged all the elements in an ascending order of atomic weights along a helix encircling a cylinder whose circumference he divided into 16 equal parts. Some elements with similar properties were found to lie one over the other along a vertical line, but this was not always the case. De Chancourtois worked on the hypothesis that the properties of the elements change periodically, each period consisting of 16 elements.

In his book "Modern Theories of Chemistry and their Significance for Chemical Statics" which was published in 1864, Lothar Meyer using new, more accurate atomic weights, made up three tables in which elements with similar valency (or atomicity as he termed it) were grouped together; in other words the chemical properties of the elements in each group were similar and there was an approximately constant difference in their atomic weights. The first table contained quadrivalent elements from carbon to lead, trivalent ones from nitrogen to bismuth, divalent ones from oxygen to tellurium, monovalent ones from fluorine to iodine, monovalent metals from lithium to caesium (Meyer included in this group also thallium, which he erroneously considered as a monovalent metal) and divalent metals from beryllium to barium. In the second table Meyer put quadrivalent titanium, zirconium and tantalum and hexavalent molybdenum, vanadium and tungsten. The third table contained quadrivalent manganese, iron, ruthenium, platinum, nickel, rhodium, iridium, cobalt, palladium and osmium, divalent zinc, cadmium and mercury, and without indicating their valency, copper, silver and gold. Meyer wrote: "Undoubtedly, there is some regular consistency in the numerical values of the atomic weights ..." without attempting to discover what this consistency might be. In the same year, 1864, Odling presented a table of the elements in his text-book of chemistry also using the new atomic numbers without indicating the principle underlying the arrangement of the elements in the table and only remarking that "the regular arithmetic ratios represented by the atomic weights are too numerous and too clear not to depend on some unknown law". Finally, one must also mention the table made up by Newlands in 1866, in which the elements were arranged in order of ascending atomic weights, eight to a row. Newlands called his table "the Law of Octaves" and noted a periodic recurrence of the elements' properties. At the same time there are obvious inconsistencies in Newland's table, such as for example the appearance of such dissimilar elements as hydrogen, fluorine and cobalt in one group.

It can thus be seen that by 1869 there were already many attempts at systematising all the then known chemical elements. Mendeleev was aware of all these attempts and divided them into artificial, i.e. formal ones, and natural ones. He assigned attempts such as Newland's octaves to the former, and those tables which were based on chemical and other properties of the elements—to the latter. This principle, which was the only correct one, also underlay Mendeleev's own system of the elements, which he rightly termed natural.

Unlike his predecessors, who could not see the general law which some of them only vaguely guessed at beyond the particular relationships noted for individual groups of elements, Mendeleev aimed right from the start at finding a general law which would be characteristic of the system of the elements as a whole. In his article "The Problem of a System of the Elements", Mendeleev wrote: "I took, with a few exceptions, the same groups of similar elements as did my predecessors, but my aim was to study the consistent features in the relationships between the groups. This led me to ..... a general principle which is applicable to

all the elements and embraces many of the previously expressed analogies, but also allows consequences which would have been formerly impossible". Speaking to the Chemical Society in England in 1889, Mendeleev said that his predecessors de Chancourtois and Newlands had "stood foremost in the way towards the discovery of the periodic law, and that they merely wanted the boldness necessary to place the whole question at such a height that its reflection on the facts could be clearly seen". It is not, of course, a question of their having lacked decisiveness and his having had the necessary daring and persistence. The discovery of the Periodic Law was the culmination of the whole of Mendeleev's earlier scientific endeavour. As his colleague, Ozarovskaya, relates, when she asked Mendeleev how his periodic system occurred to him, he said: "I have been pondering on it for perhaps twenty years".

Referring to one of his first scientific papers "Isomorphism in Connection with Other Relationships of the Crystalline Form to Composition", which he presented as a dissertation on graduating from the Principal Pedagogical Institute in St. Petersburg in 1855, Mendeleev wrote: "The writing of this dissertation involved me predominantly in the study of chemical relationships. It determined much of what was to come".

Mendeleev's particular scientific outlook and the breadth of his views and interests played an exceptional role in the fact that he was the first to see that the laws of the periodic system of the elements were of outstanding significance for the development of science. L. A. Chugaev, in characterising Mendeleev as a scientist of exceptionally wide horizons, wrote in his biographical article: "Mendeleev .... had the ability to bring a philosophical outlook to chemistry, physics and other natural sciences with which he came into contact, and a scientific experimental approach to problems in philosophy, economics and sociology". Further on Chugaev wrote: "in his endeavours to take into account the physical conditions and factors of chemical processes, Mendeleev was imperceptibly led into probing questions poised on the borders between chemistry and physics; he became interested in solutions and isomorphism, capillary phenomena, changes in state for substances and, in particular, the change in the volume of gases as a function of pressure and temperature. Work with rarefied gases opened up for him wide vistas of possible applications to meteorology; he developed a desire to probe the conditions prevailing in the upper strata of the atmosphere; he carried out remarkable work on the flow resistance of liquids, closely related to the problems of aeronautics, etc.". And further on: "With such a broad sweep of thought and many-sidedness of activity, all Mendeleev's work was both deeply pondered and carefully carried out. This became possible only thanks to his extraordinary capacity for work, which enabled him to work throughout whole nights, with hardly a few hours' rest".

While studying capillary phenomena Mendeleev discovered critical temperature which he termed "the temperature of absolute boiling". Mendeleev's studies of the compressibility of liquids, of solutions, of ammonia-metal compounds and thionic acids, as much of his other research, invariably represented new advances in science. The range of Mendeleev's scientific views and interests can be judged from his works on fuels, petroleum technology, explosives, metallurgical problems, metrology, agriculture and many other topics.

D. I. Mendeleev was born in 1834, the son of the Director of the Tobolsk Gymnasium. He entered the Gymnasium in 1841, finishing school in 1849, and in 1850 he was accepted at the Principal Pedagogical Institute in St. Petersburg. He graduated from the Institute in 1855 with a Gold Medal and was appointed to teach science in Simferopol, from which he moved to Odessa when the school in Simferopol was closed because of the Crimean War. Towards the end of 1856 Mendeleev returned to St. Petersburg. He gained his Master's degree there and defended a dissertation for the title of Privatdozent; in 1857–1858 he began teaching organic chemistry at the University of St. Petersburg. In January 1859 Mendeleev was sent abroad, to Heidelberg, for two years, returning in 1861. Whilst abroad, Mendeleev took part in the famous International Chemical Congress in Karlsruhe in 1860. When Mendeleev returned to Russia he resumed lecturing at the University. In 1861 he published his book "Organic Chemistry" which was the first Russian text-book of organic chemistry. In 1864 Mendeleev was elected Professor at the Department of Chemistry of the Petersburg Technological Institute. In 1865 he presented his doctoral thesis "The Combination of Alcohol with Water" and at the end of that year his appointment as Professor of St. Petersburg University in the Department of Technological Chemistry was ratified. In 1867 he was appointed to the Chair of General Chemistry.

In 1876 Mendeleev was elected Corresponding Member of the Petersburg Academy of Sciences. He was an honorary member of five Russian Universities. Mendeleev was also awarded honorary degrees by Cambridge, Oxford and several more of the oldest Universities of Europe. He was elected Fellow of the Royal Society of London; member of the Rome, Paris, Berlin and other Academies of Science and honorary member of many scientific Societies. In 1896 Mendeleev became head of the Principal Bureau of Weights and Measures in St. Petersburg. Mendeleev died in 1907, in St. Petersburg.

Mendeleev was convinced of the existence of a periodic law by the periodicity of the chemical properties of the elements which he had clearly demonstrated in his Natural System of the Elements in 1870, by the formulae of the higher oxides and hydrides of the elements, the regularities in the realtionships of the atomic weights of the elements in each group of chemical analogues, the periodicity in the change of specific gravities and atomic volumes, in the properties of the various compounds of the elements and in a number of their other special features.

Mendeleev was deeply convinced that the Periodic Law was objectively correct and of the utmost scientific and practical importance and he spared no effort in making it widely available to science as soon as possible. He wrote: "Each law of Nature becomes of scientific significance only if it allows, as it were, some practical consequences, i.e. logical deductions of the sort that would explain the hitherto unexplained and indicate phenomena unknown until then, and especially if the law leads to predictions which can be verified experimentally".

Mendeleev used the Periodic Law to predict the existence and properties of many of the then unknown elements. The first one was gallium, discovered by Lecocq de Boisbaudran in France in 1875, scandium, discovered by Nielsen in Sweden in 1880 and germanium, discovered by Winckler in Germany in 1886. The discovery of these elements was a triumph for the Periodic Law, and many of those who at first doubted that Mendeleev's Law was in fact general and correct, became his supporters.

The same conviction of the rightness of the Periodic Law enabled Mendeleev to alter the atomic weights of a number of elements. Thus, for example, he indicated that according to his Periodic System uranium should be hexavalent and not trivalent as had been accepted up to then, and hence the atomic weight of uranium should be 240 and not 120.

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The atomic weight of indium was similarly corrected from the previously accepted 75 to 113. The atomic weights of uranium and indium are now known to be 238.07 and 114.82 respectively.

With time the atomic weights of elements were corrected and determined more precisely, new elements were gradually discovered as predicted by Mendeleev and marked with dashes in the empty positions of his Table. Some of these elements were not discovered until many years after Mendeleev's death in 1907. Thus, rhenium (Mendeleev's bimanganese) was discovered by V. and E. Noddack, Tacke and Berg in 1925, and francium (ekacaesium) by Perey in 1939.

Mendeleev, naturally, could not have predicted the group of inert gases because of their characteristic chemical inertness. Rayleigh and Ramsay discovered argon in 1894 in England, and in 1895 Ramsay discovered helium which had been discovered as early as 1868 in the sun's atmosphere by its spectrum (Jansen and Lockyer). Ramsay was convinced that helium and argon were chemical analogues, unlike any of the known elements in their chemical properties, and therefore must constitute a separate group in Mendeleev's Table; in 1897 he therefore predicted, on the basis of the quantitative relationships of the atomic weights of the elements in each group that other elements must exist in the helium group with the atomic weights of 4(helium) + 16 = 20, 40(argon) + 44 = 84 and 84 + 44 = 128, which he and his assistant Travers subsequently discovered in the atmosphere. The new rare gases, as Ramsay named them, had the following atomic weights: 20.18 (neon), 83.7 (krypton) and 130.2 (xenon). The group of rare elements was included by Mendeleev in his Table as the zero group.

Nevertheless, neither the creation of new groups, nor the more accurate determination of the atomic weights could remove those exceptions, although not numerous, which were observed in the distribution of the elements in Mendeleev's Table. Namely, in arranging the elements in an ascending order of atomic weights, Mendeleev had to make the following exceptions: potassium, with an atomic weight of 39.10 was placed before argon with an atomic weight of 39.94, nickel (58.69) after cobalt (58.93) and iodine (126.93) after tellurium (127.61). Apart from these exceptions Mendeleev encountered difficulties in placing the rare earth elements (lanthanides). He wrote in the eighth edition of "The Fundamentals of Chemistry": "For some rare metals with the R_2O_3 type of oxides there is no place in Group III of the Periodic Table .... I have not yet found any personal interpretation of this, and it appears to me as one of the most difficult problems presented by the Periodic Law".

These and similar difficulties (especially the difficulties in arranging the actinides) were not, and could not be, solved during Mendeleev's lifetime, since the atomic weight was the only reliable characteristic of an element then available.

Several years after Mendeleev's death his Periodic Law found an ally in the theory of atomic structure which began to develop vigorously from 1911, when Rutherford discovered the atomic nucleus. The next important step along the path of discovery of atomic structure and establishment of a connection between the structure of the atom and the Periodic Law was made by Moseley in 1913. Moseley studied the X-ray spectra of various elements and as a result of these established a simple connection between the wave length of certain lines of the characteristic X-ray spectra of the elements and their atomic number, which Moseley correctly identified with the nuclear charge, expressed in units of elementary charge. The truth of this conclusion was substantiated a little later in the very first experiments on alpha-particle scattering performed by Chadwick in Rutherford's laboratory. These experiments gave values for the nuclear charge in the atoms of copper, silver and platinum (29.3, 43.3 and 77.4) which coincided, within the limits of experimental error, with the atomic numbers of these elements in Mendeleev's Table (29, 47 and 78 respectively). It followed from this, and from later experiments, that the nuclear charge was always equal to the atomic number of the element in the periodic system.

It is also noteworthy that the experiments carried out by Barkla and others on X-ray diffraction by various elements revealed that for all the light elements investigated, the nuclear charge was equal to half the atomic weight. If a difference between half the atomic weight and the atomic number of the element amounting to 0.5 or less is taken to be negligible, then half the atomic weight is equal, with this degree of accuracy, to the atomic number from helium to argon, and only starting with argon does the atomic weight increasingly outstrip (twice) the atomic number of the element. The arrangement of the elements in a periodic table according to their atomic weight, as made by Mendeleev and his predecessors (before atomic numbers and their physical significance were known) acquired a theoretical basis only for the first three periods in the periodic system. The discovery of atomic numbers and the development of the atomic theory provided the Periodic Law, for the whole series, with a new and definitive formulation: the properties of the chemical elements show a periodic change related to their atomic number.

If the theory of atomic structure proved to be an ally of the Periodic Law, the periodic system from its side played an exceptionally important role in the development of the atomic theory. Moreover, the question of atomic structure itself arose only after the discovery of the Periodic Law. Nevertheless, the "bricks" from which the atom could be built up only became known some 30 years after the discovery of the periodic system of the elements. The concept of elementary electric charge was first formulated clearly by Helmholtz in 1881, but the electron itself—one of these "bricks", was only discovered by J. J. Thomson in 1897. The other "brick"—the atomic nucleus, as already mentioned, was discovered by Rutherford in 1911. Following the discovery of radioactivity (Becquerel, 1896) and the formation of helium as the result of radium decay (Ramsay and Soddy, 1903) it became evident that the elements could be transmuted one into the other, thus confirming the genetic interconnection of the elements, their mutual kinship. In 1913 Niels Bohr put forward the theory of the hydrogen atom. The hydrogen atom, with its electron levels, proved, in a sense, to be a prototype of all the elements in the periodic system. In 1924 Born and Heisenberg extended the theory of the hydrogen atom to the alkali metal atoms. In 1926 Heisenberg, using quantum mechanics as a basis, solved the problem of the helium atom, and then between 1926–1930 the theoretical problem of the atom with many electrons was solved.

The Pauli exclusion principle (1925), according to which an atom cannot have more than one electron characterised by the same set of four quantum numbers, the number n being able to have the values of 1, 2, 3, 4 etc., the quantum number l which can have values 0, 1, 2 ... $(l - 1)$, the quantum number m which can have values l, $(l - 1)$ ... $-l$ and the quantum number s which can be $+\frac{1}{2}$ or $-\frac{1}{2}$ (inserted by Ed. of Translation), the position of the electron in the atom is determined. This set of quantum numbers, together with Pauli's principle and the postulate that the

ground state of each atom is the state with the lowest energy, give the physical foundations of the periodic system of the elements. It follows from the values established in the quantum atomic theory and the relationship of the quantum numbers and the Pauli principle that, for a given value of the so-called principal quantum number n, which may be 1, 2, 3, 4, etc., the maximal number of electrons in an atom cannot exceed the value $2n^2$, i.e. 2, 8, 18, 32 etc. These electrons form a closed electron shell and are distributed among subgroups with the maximal number of electrons in each orbital being equal to $2(2l + 1)$ where the quantum number l has the values 0, 1, 2 ... $(n - 1)$. The electrons with the quantum numbers $l = 1$, 2, 3 etc. are called s-, p-, d-, f- etc. electrons, respectively.

It follows from the above formulae that the single-quantum shell of the atom ($n = 1$) contains two s-electrons. This shell cannot accommodate more than two electrons and is therefore a closed electron shell which is first filled in helium the atom and then remains unchanged throughout Mendeleev's Table. The two-quantum shell can accommodate six p-electrons in addition to the two s-electrons. This gives a second closed eight-electron shell, which is completed in neon and remains, like the single-quantum shell, closed throughout the Mendeleev Table. The next, three-quantum, shell contains a maximum of 18 electrons: two s-electrons, 6 p-electrons and 10 d-electrons. It was found that only the heavier elements, starting with copper (atomic number 29), possessed the maximal number of electrons, viz. 18. In the three lighter elements, argon, potassium and calcium (atomic numbers 18, 19 and 20) the still incomplete eight-electron third shell already showed the properties of a closed shell, as witnessed by the chemical and physical properties of the Ar atom and the K^+ and Ca^{++} ions.

This and similar facts can be explained as follows. In passing from an element with the atomic number N to the next heavier element N + 1, i.e. with an increase in the nuclear charge and the number of electrons by unity, the "(N + 1)-th" electron occupies the lowest possible energy level. The observed sequence of filling the electron orbitals of the first 20 elements (ending with Ca) indicates that the 19th electron in potassium and the 20th electron in calcium are not d-, but s-electrons, i.e. they are placed in the four-quantum shell which corresponds to the lowest energy; this also follows from the theoretical model of the K and Ca atoms. The d-orbital of the three-quantum shell only begins to fill starting with the next element, scandium (atomic number 21), which is complete in copper, as has already been mentioned. The irregularity with which this orbital is filled, determined each time by minimizing the energy of the atom, explains all those anomalies which are observed in the properties of the elements from scandium to copper. A similar irregularity in the filling of electron orbitals underlies the anomalies in the elements from yttrium to palladium, in the rare earth elements—from the 58th element, cerium to the 70th, ytterbium in which the 32-electron shell with $n = 4$ is first completed, and in the group of heavy elements starting with actinium (atomic number 89).

The discovery of isotopes and the insight into the structure of atomic nuclei played a significant part in the understanding of the structure of the system of the elements and the relationship between the atomic weight and the atomic number of the elements. The problem of the isotopes first arose after the discovery of radioactive elements—the number of products of the radioactive decay of uranium and thorium exceeded the number of free places in Mendeleev's Table. The only course open was to place the elements with similar chemical properties but different atomic weights into one space. Soddy, in 1910, called such variants of the element isotopes. It is interesting to note that the thought of the possible existence of isotopes had been voiced, in passing, by a number of nineteenth century scientists. Thus, for example, Butlerow, addressing the Russian Physico-Chemical Society in 1881 said: "... Most atomic weights approximate whole numbers to such an extent that it can hardly be considered fortuitous. Could it not be supposed that under certain conditions atomic weights might actually be expressed by whole numbers (related to H = 1), i.e. that the atomic weights represent values which, under certain conditions, can change within certain limits?" Isotopes proved not to be an exclusive feature of radioactive elements only. Already in 1912 J. J. Thomson found that there were two varieties of neon atoms, with atomic weights 20 and 22. Now we know that each element consists of a certain number of stable and radioactive isotopes.

It is also known that in addition to isotopes there are also isobars—isotopes of different elements which, however, have the same atomic weight. Their existence demonstrates particularly clearly that it is not the atomic weight but the atomic number of an element, i.e. the nuclear charge and hence the number of electrons in the atom, which determines the chemical and other properties of the element. In particular, the chemical properties of the elements, according to the atomic theory, are determined by the outer electrons of the atom and their energetics. The periodicity of the chemical and other properties of the elements is a direct consequence of the periodicity in the arrangement of the orbitals and sub-orbitals in the electron shells of the atoms.

Isotopes also played a big part in the creation of the theory of the atomic nucleus which, in turn, was of the greatest significance in interpreting the structure of the periodic system of the elements, in particular the relationship between the atomic weight and the atomic number of the elements. Nuclear forces acting between the nucleons—the component parts of the nucleus, protons and neutrons, which at a certain ratio between the number of protons and neutrons bind them into a whole—the atomic nucleus. However, besides the forces of attraction between the protons in the nucleus there are also forces of electrostatic repulsion, which make the nucleus less stable. When the number of protons in the nucleus is small the nucleus may remain stable even with an excess of protons since the nuclear forces are several times stronger than the repulsive forces. The light isotope of helium ^3He has such a nucleus, which consists of one neutron and two protons. The isotopes of all the elements following helium, however, are unstable when the number of protons exceeds the number of neutrons and this explains the fact that the higher the atomic number of the element, i.e. the larger the number of protons, the more does the number of neutrons in the nucleus of its stable isotopes exceed the number of protons.

We can thus see that the theory of atomic structure, of its electron shells and its nucleus, proved to be the physical basis upon which the periodic system of the elements rests. All the difficulties in arranging the elements within the system and the contradictions which arose during the first stages of constructing the system disappeared in the light of the atomic theory. At present the periodic system of the chemical elements forms the foundations on which rests all our science, the guiding light illuminating the progress of science in the future.

The role of the Periodic Law in the advancement of science was utterly clear to Mendeleev from the first years

of the existence of his periodic system of the elements. Addressing the Chemical Society in England in 1889 he referred to the Periodic Law as an "instrument of enlarging our mental horizon" and said that "the law of periodicity enabled us to perceive undiscovered elements at a distance which formerly was unaccessible to chemical vision".

The Periodic Law gave an impetus to the advance of inorganic chemistry. It had an enormous and decisive significance for the development of the atomic theory and the atomic nucleus, for nuclear physics and nuclear chemistry. It is exceptionally important for the development of geochemistry, geology, crystallography, mineralogy and metallurgy. It is a guiding light in catalysis and the consideration of the rates of chemical reactions. There is no branch of science where the Periodic Law does not exert its influence.

The whole world celebrates gratefully the centenary of Mendeleev's achievement and recalls the names of all those whose endeavours and genius have put before us the Periodic Law in all its majesty and brilliance.

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Kinetics and Mechanism of Three-body Recombination of Atoms and Radicals

A.D.Stepukhovich and V.M.Umanskii

The review gives a general account of the results of numerous studies on the simplest atomic and radical reactions which are experimentally found to follow third-order kinetics. A large number of experimental results, arranged systematically in tables and graphs, are quoted and discussed. The principal characteristics of the properties of the reactions of this class (negative temperature dependence of the rate constant, different efficiencies of third bodies, relation between the efficiency and structure, etc.) are analysed. The possible interpretation of these processes on the basis of the simplest theoretical postulates—kinetic collision theory, theory of absolute reaction rates, and other equilibrium theories—are considered.
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I. INTRODUCTION

The hypothesis that elemenatry trimolecular reactions should be encountered very rarely because of the low probability of true three-body collisions arose already in the early stage of the development of chemical kinetics. Thus, according to Trautz [1], trimolecular reactions of the type A + B + C → product do not exist and pseudotrimolecular processes actually involve a complex mechanism: (1) A + B ⇌ AB; (2) AB + C → product. The rate-determining stage in the complex process is the second reaction, which does not affect the rapidly established equilibrium of the first stage. The kinetics of the oxidation of NO and of the formation of nitrosyl bromide and chloride were in fact interpreted from this standpoint.

The statistical calculations of Bodenstein [2], Tolman [3], Kassel [4], and Steiner [5-7] showed that, despite certain difficulties, a quantitative treatment of such reactions is indeed possible on the basis of the hypothesis that a three-body collision takes place in two stages: initially a pair (doublet) is formed and then a triplet following the approach of a third particle. Kassel [4] showed that, by taking into account the interaction between real gas molecules, it is possible to explain the characteristics of the temperature variation of the rate constant of a trimolecular reaction. The rate constant is written in the traditional form:

$$k = z_{\text{eff}} = Ae^{-E/RT} = ze^{-E/RT} \quad , \qquad (1)$$

where A and E are the pre-exponential factor and the activation energy for the trimolecular reaction and z, the number of three-body collisions per cm^3 per second, is calculated from the formulae of Tolman or Kassel:

$$z = 8\sqrt{2}\,\pi^{3/2}d_{12}^2 d_{23}^2 \delta \sqrt{kT}\left(\frac{1}{\sqrt{\mu_{12}}} + \frac{1}{\sqrt{\mu_{23}}}\right) N_1 N_2 N_3 \quad , \qquad (2)$$

$$z = 8\pi l_0^2 \sqrt{\frac{2\pi kT}{\mu}}\left(1 + \frac{\varphi_0}{kT}\right)\left[\int_0^{\rho_0} e^{-E(r)/kT} r^2 dr\right] N_1 N_2 N_3 \quad , \qquad (3)$$

where d_{12} and d_{23} are the gas-kinetic diameters of the doublets, μ_{12} and μ_{23} their reduced masses, N_1, N_2, and N_3 the numbers of molecules per cm^3, l_0 the distance between the particles forming the doublet, ρ_0 the distance between the centre of gravity of the doublet and the third particle, φ_0 the potential energy of the doublet, and $E(r)$ the potential energy at a distance r.

In the theory of equilibrium reaction rates [8,9] the formation of an activated complex from the free reacting molecules also may be preceded by a stage of the equilibrium formation of the binary complex AB with the subsequent formation of the trimolecular complex ABC as a result of the addition of the particle C (AB + C → ABC). The fundamental hypothesis is that equilibrium exists between the complex ABC and the initial reactants, the first equilibrium stage not affecting the equilibrium between the activated complexes and the starting materials A, B, and C. This permits a formal representation of the complex process as an elementary trimolecular reaction. Since three-body collisions between particles occur very rarely, it follows that, for trimolecular reactions to have rates which can compete with bimolecular reactions under certain conditions, they must have low activation energies or actually negative temperature coefficients, as happens in three-body recombination. The hypothesis that simple trimolecular reactions exist has become firmly established in chemical kinetics in connection with the study of the simplest process—the formation of diatomic molecules by the recombination of the atoms (H, O, Br, I, and others). By analysing the potential energy curves for the interaction between atoms, Born and Franck [10], Herzfeld [11], and Polanyi [12] showed that the formation of a stable molecule by the recombination of atoms requires the collision of the mutually approaching atoms with a third particle capable of absorbing the excess energy of the molecule just formed and thus enabling it to be stabilised "in the potential well"†. The transfer of excess energy from the excited molecule to the third particle may depend on the structure of the latter, in particular on the presence in its energy spectrum of resonating levels capable of accepting the excitation energy (vibrational or electronic energy) of the molecule in a collision of the second kind. This may account for specific effects of third bodies, without resorting to hypothesis that the specificity is due to the formation of complexes or intermediate compounds between one of the atoms or radicals and an external particle. The specificity of the effect then follows from the characteristics of the transformation and transfer of the energy of the excited particle, i.e. the transformation of its energy into one of

†Boltzmann [13] drew attention to this even earlier.

the forms of the internal energy of the third particle (vibrational, rotational, etc.), which means that the specificity follows from purely physical considerations. The mechanism of the recombination of atoms or radicals via energy transfer to a third particle is sometimes called in modern literature the "ET mechanism" (the energy transfer mechanism) [14].

The experimental study of the rate constants for three-body recombination of atoms shows that at moderate temperatures they are generally of the order of 10^{15} cm^6 $mole^{-2}$ s^{-1} and are characterised by low negative temperature coefficients, i.e. low negative activation energies in the range 0–5 kcal $mole^{-1}$. However, in some cases much higher rate constants have also been obtained experimentally for atomic three-body recombination reactions, indicating the specificity of the effect of third bodies. These data could not be explained within the framework of the ET mechanism. Furthermore, this mechanism, when applied to the specific effect of third bodies, had already encountered serious criticism in the early work of Rabinowitch [15]. A radical–molecular complex mechanism, called for brevity the RMC mechanism, has been proposed to explain the existence of more powerful effects of third bodies on the recombination of atoms or radicals. In three-body recombination reactions of atoms or radicals involving an RMC mechanism, the participation of a third particle in the process involves its ability to form reversibly with one of the radicals intermediate complexes having an excess excitation energy. This energy may be evolved in collisions between the excited complex and the third particle, after which the normal complex interacts with the radical to yield the product and the chemically unchanged third body. The RMC mechanism can provide a natural explanation of the specific effect of third bodies through the concept of reaction complexes, i.e. within the framework of the concept of homogeneous catalysis, which may accelerate the recombination and can account for the widespread occurrence of recombination with participation of third bodies, which play the role of process catalysts.

The question of the competition between ET and RMC mechanisms in each particular case can be resolved in principle by comparing the lifetimes of the corresponding intermediate species [14]. For example, in the recombination of atoms in the presence of fairly complex (or chemically active) third bodies the intermediate compound of the atom and the third body may be longer-lived thereby facilitating the reaction by the complex mechanism; on the other hand, the recombination of complex radicals in the presence of a simple third body will evidently be faster when the ET mechanism operates. However, these are unusual "limiting" cases. It may be that the lifetimes of the complex formed in the first stages of both mechanisms are comparable on *a priori* grounds and it is difficult to decide qualitatively what are the true relative contributions of the recombination mechanisms (for example in reactions with participation of simple unsaturated molecules).

Below we shall discuss in greater detail the experimental data for three-body recombination reactions of atoms and radicals on the basis of the collision theory, the theory of absolute reaction rates, and certain modifications of these theories.

II. EXPERIMENTAL DATA FOR THREE-BODY RECOMBINATION

During the past ten years special reviews have been devoted to experimental studies on three-body recombination reactions of atoms [16–19]. The most important general features of chemical processes of this type are discussed in the present review. We shall not be concerned with the problem of the three-body recombination of charged particles (ions and electrons), about which many experimental and theoretical papers have also been published recently [20–27,31].

The principal difficulty in the study of three-body recombination is usually the problem of obtaining a fairly high concentration of free atoms. The rapid increase of the number of studies on the kinetics and mechanism of three-body recombination from the middle of 1950's up to the present time is mainly due to the successful assimilation of new effective methods for the production of free atoms. These are flash photolysis [28–31] and the method of shock tubes [31–33]. While the method of flash photolysis permits the direct measurement of the rate constant for the recombination of atoms, in shock tube experiments measurements are made (at high temperatures) of the reverse reaction, i.e. thermal dissociation, and the results must be recalculated in terms of equilibrium constants. Flash photolysis alone is applicable over a fairly narrow range of low temperatures. However, the combined use of flash photolysis together with the shock tube method permits [34] measurements of the rate of recombination at much higher temperatures (the shock tube being used to heat the dissociation gas).

The two methods described are at present the most important in the study of dissociation and recombination processes. Apart from these, the free atoms of light elements are frequently produced by an electrode or electrodeless gas discharge (see for example papers by Canadian workers [35–39]). There exist also a number of different methods for the recording of the concentrations of atoms. Among these the ESR method [40,41], the method of "titration" using a rapid side reaction [42–46], and others have found successful application.

1. Absolute Rate Constants for Three-body Recombination of Atoms‡. Effectiveness of Various Particles as Third Bodies

The interest in three-body recombination reactions of atoms arose to the first place in connection with the problem of the recombination of hydrogen atoms. In the 1930's an extensive series of measurements of the rate constant for this reaction was made close to room temperature (Table 1). The results of these measurements show marked discrepancies because of the imperfection of the method under both static and flow conditions. Nevertheless a great achievement of these early studies was the formulation of the problem of the relative efficiencies of various particles as "third bodies" in the recombination process. However, the initial data on this problem proved to be extremely contradictory: while Steiner in several experimental and theoretical studies [5–7] insists that the

‡The available literature data for the rates of three-body recombination of identical atoms are expressed in two different ways: either in terms of the accumulation of molecules, $d[A_2]/dt = k[A]^2[M]$, or in terms of the consumption of atoms, $-d[A]/dt = k'[A]^2[M]$, where $k' = 2k$. In the present review all the numerical constants refer to the first equation, i.e.

$$k = \frac{1}{[A]^2[M]} \frac{d[A_2]}{dt}.$$

hydrogen atom is less effective than the hydrogen molecule (k_H is not more than 10% k_{H_2}), Senftleben and Reichemeier [47,48] quote $k_H/k_{H_2} \simeq 2000$. At the same time in a series of papers Amdur [49-53] asserts that the effectiveness of the H and H_2 species is comparable and that there are no grounds for expecting a significant difference between them.

Table 1. Rate constants for the recombination of hydrogen atoms: $k = \frac{1}{(H)^2(M)} \frac{d(H_2)}{dt}$.

Room temperature (293-298°K)				High temperatures* (from experiments on dissociation of H_2 in shock tubes)			
third body M	k, $cm^6\ mole^{-2}\ s^{-1}$	$\frac{k_H}{k_{H_2}}$	references	third body M	k at 3500°K, $cm^6\ mole^{-2}\ s^{-1}$	$\frac{k_H}{k_{H_2}}$	references
H H_2	$1.3 \cdot 10^{16}$ $2.8 \cdot 10^{16}$	0.47	57	H H_2 Xe	$3.0 \cdot 10^{15}$ $1.3 \cdot 10^{14}$ $4.5 \cdot 10^{14}$	23	63
H	$\sim 1.7 \cdot 10^{17}$	$2 \cdot 10^3$	48	H H_2 Xe	$2.2 \cdot 10^{15}$ $9.2 \cdot 10^{13}$ $3.3 \cdot 10^{14}$	24	64
H_2	$9 \cdot 10^{15}$	~ 0.1	5	H H_2 Ar	$8.7 \cdot 10^{15}$ $7.1 \cdot 10^{14}$ $1.7 \cdot 10^{14}$	12	65
H_2	$1.6 \cdot 10^{16}$	0.25-1.0	49	H H_2 Ar	$9.5 \cdot 10^{15}$ $7.3 \cdot 10^{14}$ $1.7 \cdot 10^{14}$	13	66
H	$8.5 \cdot 10^{15}$	>50	58	D** D_2** Ar**	$5.8 \cdot 10^{15}$ $1.4 \cdot 10^{14}$ $2.3 \cdot 10^{14}$	41	66
H_2 H, Ar	$1.7 \cdot 10^{16}$ $5.6 \cdot 10^{15}$	0.3	59				
H	$1.02 \cdot 10^{16}$	$\geqslant 10$	52	H H_2 Ar, Kr, Xe	$2.9 \cdot 10^{15}$ $8.6 \cdot 10^{14}$ $4.3 \cdot 10^{14}$	3,4	67
H_2	$5.5 \cdot 10^{15}$	$\leqslant 0.1$	7				
H_2	$1.0 \cdot 10^{15}$		60				
H_2 H_2 H_2	$0.9 \div 1.2 \cdot 10^{16}$ $1.18 \cdot 10^{16}$ $8.9 \cdot 10^{15}$		53 40 61	H H_2 Ar	$1.4 \cdot 10^{16}$ $2.1 \cdot 10^{15}$ $2.1 \cdot 10^{14}$	6,7	68
NO	$1.1 \cdot 10^{16}$		62	Ar	$4 \cdot 10^{14}$***		69

*Most investigators [65-68] who measured the rate of recombination over a fairly wide range of temperatures (mainly 3000-5000°K) noted a decrease of the rate constant, on raising the temperature, in accordance with a T^{-1} law when M is an inert gas. However, Gardiner and Kistiakowsky [64] failed to observe any significant temperature variation in the range 3000-4500°K.

**The values quoted refer to the recombination of deuterium atoms.

***This value was obtained at 1700°K.

It follows from general theoretical considerations [9,54] that a third body M capable of chemical interaction with the recombining atoms (which is the case when M = H) should as a rule constitute a more effective third body. When applied to the reaction under consideration, this point of view is satisfactorily confirmed by later experiments at high temperatures (Table 1, see also Dixon-Lewis et al. [55]) the more self-consistent results of which show that k_H exceeds k_{H_2} on the average by one power of ten. This apparently contradicts the self-evident physical consideration that a larger number of degrees of freedom in the particle M should favour a more effective removal of energy from the recombining pair during its stabilisation in a three-body collision, increasing thereby the rate constant [56]. However, this is true only when particles M which are chemically inert to the recombining particles are compared. In this case the formation of a fairly stable compound H_3 in the interaction between H and H_2 is unlikely (H_2 may be regarded as an inert third body); therefore the above qualitative estimate is inapplicable and the high effectiveness of H as the particle M becomes quite understandable (see also for comparison the data on the recombination of atomic oxygen in Table 2).

The recombination of iodine and bromine atoms has been fairly thoroughly investigated over a wide range of conditions (Tables 4 and 6-8). In practice the role played by the three-body recombination reactions of halogen atoms in photochemical reactions of the type $H_2 + X_2 \rightarrow$ product, where X_2 is a halogen, is very important. The first data on the recombination Br + Br + M → product were in fact obtained by studying the kinetics of the photochemical reaction between H_2 and Br_2. [70-74] The classical experiments of Rabinowitch and coworkers [75-79], designed to investigate the photochemical steady states, marked the beginning of the systematic investigation of the three-body recombination of halogen atoms (iodine and bromine). In these experiments the wide differences between the effectiveness of various atoms and molecules as third bodies were noted for the first time, the absolute values of the rate constants (on the average 10^{15} $cm^6\ mole^{-2}\ s^{-1}$) proving significantly higher than would follow from initial theoretical estimates by Bodenstein [2]. At the same time Rabinowitch [15] suggested that the very high effectiveness of certain complex molecules (he used benzene in his experiments) may be attributed to the formation of a relatively stable atomic-molecular complex.

The dependence of the rate constant on the molecular complexity of the inert third body, mainly on the number of its degrees of freedom responsible for the energy transfer, was particularly clearly demonstrated in the work of Russell and Simons [80]; these workers quote rate constants for the recombination of iodine in the presence of more than thirty different inert gases (Table 4). For example, toluene proved to be 60 times more effective and mesitylene 110 times more effective than argon. Russell and Simons [80] made another interesting observation: they noted that the rate constants vary regularly with the boiling point, critical temperature, and ionisation potential of the inert gas, i.e. with the parameters characterising the strength of intermolecular forces. Fig. 1 illustrates this relation for the variation of $\lg k$ with the boiling point of the substance M as an example.

The existing data for the rates of recombination of the atoms of various halogens on contact with the same inert gas species show that the rate constants are higher for heavier atoms but the differences are not very great. The rates of recombination of I and Br atoms on contact with the same third body are virtually the same over a wide range of experimental conditions [81].

A large number of experimental studies on three-body recombination were stimulated also by interest in the study of chemiluminescence in gases: for example, Berkowitz et al. [82] showed that the intensity of the yellow luminescence of nitrogen depends on the consumption of free N atoms by a third-order rate law with a velocity constant of 7×10^{14} ($\times 10^{\pm 2}$) $cm^6\ mole^{-2}\ s^{-1}$ (see also Reeves et al. [83]); the greenish yellow luminescence of air is due [84] to a trimolecular reaction with participation of O and NO; the

Table 2. Rate constants for the recombination of oxygen atoms and the formation of ozone in three-body collisions.

Low temperatures									High temperatures				
$O+O+M \rightarrow O_2+M^*$				$O+O_2+M \rightarrow O_3+M$					$O+O+M \rightarrow O_2+M$				
T, °K	third body M	k, $cm^6\ mole^{-2}\ s^{-1}$	refs.	T, °K	third body M	k, $cm^6\ mole^{-2}\ s^{-1}$	Type of temp. variation	refs.	T, °K	third body M	k, $cm^6\ mole^{-2}\ s^{-1}$	Type of temp. variation	refs.
350	O_2	$3 \cdot 10^{14}$	86	296	O_2	$7.9 \cdot 10^{13}$	$\propto e^{\frac{600}{RT}}$	89	3500	O_2	$2 \cdot 10^{14}$		94
300	O_2	$5 \cdot 10^{15}$	41	296	O_3	$1.8 \cdot 10^{14}$		89	3500	O_2, Xe	$2 \cdot 10^{14}$		95
300	O_2	$1.0 \cdot 10^{14}$	35	296	N_2	$7.4 \cdot 10^{13}$		89	3500	O	$9.9 \cdot 10^{14}$		96
300	NO	$1.85 \cdot 10^{16}$	37	296	CO_2	$1.9 \cdot 10^{14}$		89	3500	O_2	$4.8 \cdot 10^{14}$		96
300	O_2	$1.03 \cdot 10^{15}$	83	296	He	$6.1 \cdot 10^{13}$		89	3500	Ar	$4.5 \cdot 10^{13}$		96
300	O	$3.2 \cdot 10^{15}$	38	296	O_2	$4 \cdot 10^{14}$		84	3500	O_3	$8.4 \cdot 10^{14}$	$\propto T^{-2}$	97
350	O_2	$\leqslant 2 \cdot 10^{14}$	87	296	O_2	$4 \cdot 10^{14}$		90	3500	O	$1.4 \cdot 10^{15}$		98
296	O_2	$1.0 \cdot 10^{14}$	88	350	O_2	$1.1 \cdot 10^{14}$		87	3500	O_2	$4.6 \cdot 10^{14}$	$\propto T^{-0,5\div-2}$	98
300	O	$8.1 \cdot 10^{14}$	40	283	O_2	$6.0 \cdot 10^{14}$		91	3500	Xe	$1.3 \cdot 10^{14}$		98
300	N_2	$1.0 \cdot 10^{14}$	39	300	O_2	$\sim 1.0 \cdot 10^{15}$	$\propto e^{\frac{1800}{RT}}$ or $T^{-3\,4}$	92	3500	O	$1.3 \cdot 10^{15}$		99
300	Ar	$\leqslant 3 \cdot 10^{14}$	39	273	Ar	$2.8 \cdot 10^{14}$		93	3500	O_2	$1.6 \cdot 10^{14}$		99
300	He	$3 \cdot 10^{14}$	39						3500	Ar	$5.2 \cdot 10^{13}$		99
300	N_2O	$1.4 \cdot 10^{14}$	39						3500	Ar	$2.3 \cdot 10^{13}$	$(\propto T^{-1})$	100
300	CO_2, SF_6	$3 \cdot 10^{14}$	39						3500	Kr	$4.6 \cdot 10^{13}$	$\propto T^{-0,5}$	100
300	H_2O	$\sim 5 \cdot 10^{15}$	39						2000	Ar	$2.5 \cdot 10^{13}$	$\propto T^{-1.2}$	101
									2200	O_2	$6.8 \cdot 10^{14}$		102**

*In Kaufman's review [18] $k = 9.8 \times 10^{14}$ was adopted as the best value for $O + O + O_2 \rightarrow 2O_2$ at room temperature. This is lower by a factor of five than the value obtained by extrapolation of the results of measurements in shock tubes.

**The method developed by Kiefer and Lutz [102] permitted the direct measurement of the rate of recombination in shock tubes, instead of its calculation from the rate of the reverse reaction via the equilibrium constant.

intensity of the red-orange luminescence arising from the products of an electric discharge in chlorine also follows a trimolecular law, $\mathcal{J} = k(Cl)^2(Cl_2)$, the $Cl_2(A^3\Pi_{1u}^+)$ molecule being identified as the source of the luminescence [85]. The study of such systems, mainly by producing free atoms from a discharge, has yielded important data on the rates of recombination of oxygen and nitrogen atoms (Tables 2 and 3). The tables also present the results of experiments in shock tubes.

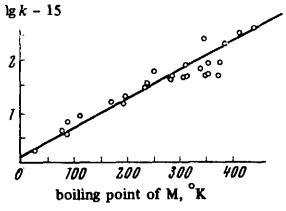

Figure 1. Variation of the rate constant for the recombination of iodine atoms with the boiling point of the substance M. [80]

Examination of the rate constants for the three-body recombination of oxygen atoms at low temperatures (Table 2) shows that they are of the order of 10^{14}–10^{15} when M is an inert gas. Kaufman [18] believes that the best value is 9.8×10^{14} for M = O_2 at room temperature. As the temperature rises, there is a tendency for the constant to fall, which is clearly demonstrated by the results of experiments in shock tubes. The specific effects of various third bodies are also clearly revealed. Table 2 lists the experimental rate constants for the formation of ozone: on the average they are somewhat smaller and are of the order of 10^{13}–10^{14}.

Table 3 lists the rate constants for the recombination of nitrogen atoms on contact with various third bodies. Their order of magnitude differs little from the corresponding values for the recombination of oxygen atoms (at low temperatures), but they vary less markedly with temperature.

Table 3. Rate constants for the recombination of nitrogen atoms*.

T, °K	Third body M	k, $cm^6\ mole^{-2}\ s^{-1}$	Type of temp. variation	Refs.	T, °K	Third body M	k, $cm^6\ mole^{-2}\ s^{-1}$	Type of temp. variation	Refs.
300	N_2, Ar	$6.24 \cdot 10^{15}$		42	298	N_2, N	$2.0 \div 3.5 \cdot 10^{14}$	$dk/dT \geqslant 0$	104
297	N_2	$2.7 \cdot 10^{15}$		43	300	N_2	$5.4 \cdot 10^{15}$		40
297	Ar	$1.6 \cdot 10^{15}$	$dk/dT \leqslant 0$	43	300	N_2	$8.0 \cdot 10^{14}$		61
297	He	$4.0 \cdot 10^{14}$		43	293	N_2	$1.38 \cdot 10^{15}$		105
300	O_2	$6.0 \cdot 10^{15}$		103	293	Ar	$1.9 \cdot 10^{15}$		105
195—400	N_2	$5.7 \cdot 10^{15}$	$dk/dT \simeq 0$	44	293	He	$1.73 \cdot 10^{15}$		105
297	Ar	$2.8 \cdot 10^{15}$		44	3000	Ne	$6.5 \cdot 10^{14}$		106
297	He	$8.2 \cdot 10^{14}$		44	3000	Ar	$3.2 \cdot 10^{14}$	$\propto T^{-0.5}$	106

*The table shows that most investigators found a very small temperature coefficient for this reaction. In the earliest experiments of Forst et al. [107] it was found that $k \propto T^{-4}$ for M = CH_3Cl and CH_3CN.

2. Three-body Recombination involving Di- and Triatomic Particles

Compared with the recombination of atoms, trimolecular reactions in the gas phase with participation of di- and tri-atomic particles, which play an important role in many atmospheric processes, chemiluminescence, and others,

have been less thoroughly investigated and information about them has begun to accumulate mainly in recent years (Table 8). Among processes in this category, the reaction $H + O_2 + M \rightarrow HO_2 + M$, which plays a major role in the kinetics of complex chemical processes, has been most thoroughly investigated. For example, the phenomenon of the upper explosion limit in the chain process of hydrogen combustion and also the classical example of the inhibition of the photochemical reaction between H_2 and Cl_2 by the addition of oxygen are in fact associated with this reaction. The inhibiting effect of O_2 is explained by the fact that the active chain radical (the H atom) combines with O_2 in a three-body collision, yielding the relatively inactive HO_2 radical, which cannot regenerate the H atom at low temperatures [108,109].

Table 4. Effectiveness of various third bodies in the recombination of iodine atoms at room temperature*.

Third body, M	$10^{-15}k$, cm^6 $mole^{-2}$ s^{-1}	Refs.	Third body, M	$10^{-15}k$, cm^6 $mole^{-2}$ s^{-1}	Refs.
Helium	3.3	79	Carbon monoxide	5.42***	122
	1.70	80	Hydrogen iodide	28.1***	122
	3.14	120	Methane	22	79
	1.21	121		8.89	80
	1.41	122	Methyl iodide	150	122
	1.52	123	n-Propane	30.5	80
Neon	1.81	80	Cyclopropane	39.5	80
	3.37	120	n-Butane	35.0	127
	1.67	121	n-Pentane	47.0	79
	1.9**	124	Neopentane	58	125
Argon	6.9	79	2,2-dimethylpropane	43.5	80
	3.63	80	Cyclohexane	54.4	80
	4.39	120	Ethylene	17.1	80
	3.34	121	Tetrafluoroethylene	21.0	80
	4.2	125	Trifluorobenzene	87.8	80
	4.5	126	Benzene	180	79
	2.90	127		87.1	80
	3.65	128		100	122
	2.97	123		79.6	123
Krypton	6.18	120	Toluene	210	80
	4.08	121		194	123
Xenon	6.24	120	Azomethane	187	80
	5.42	121	*p*-Xylene	332	80
Hydrogen	7.3	79	Mesitylene	406	80
	4.77	80		405	123
	4.93	122	Iodine	853	121
Nitrogen	12.0	79		1720	127
	4.52	80		1380	123
Oxygen	19.0	79	Methanol	64.9	80
	6.66	80	Methyl ether	61.9	80
	6.75	123	Methylene dichloride	47.7	80
Water	49.7	80	Carbon tetrachloride	50.8	80
Carbon dioxide	33	79	Ethyl chloride	47.7	80
	13.5	80	Ethyl bromide	80.2	80
	13.4	123	Ethyl iodide	250	80
Nitric oxide	>4.8·10⁶***	122		238***	122
	3·10⁴**	124		261	123

*The results of some studies [79,80,120,125,128] were not corrected for the rapid reaction $2I + I_2 \rightarrow 2I_2$. Therefore the rate constants for relatively ineffective third bodies may deviate from the true values.

**Measured at 60°C

***The values for 50°C are quoted. When M = NO, the rate of reaction is too high for a reasonably accurate determination of the constant.

The $H + O_2 + M \rightarrow$ product reaction was investigated by many workers [110–118] and experimental constants for this reaction, in good mutual agreement, are now available: measurements of Clyne and Thrush [113] in the range 250–800°K and of Getzinger and Schott [115] in the range 1150–1850°K. An interesting feature of this reaction [109,118,119] is a very pronounced catalytic effect of water vapour ($k_{H_2O}/k_{Ar} \simeq 30$ and hardly changes with temperature). This makes it difficult to investigate the upper limit (and particularly its temperature variation), since the presence of even small traces of water vapour in the reaction zone can significantly lower it. Semenov [108] believes that in this case there is a possibility of an unusual chemical interaction involving the formation of the complex $H.H_2O$.

Table 5. Rate constants for three-body recombination involving di- and tri-atomic species.

Reaction	Third body M	T, °K	k, cm^6 $mole^{-2}$ s^{-1}	Type of temp. variation	References
$H + O_2 + M \rightarrow HO_2 + M$	H_2	293	$\sim 1.3 \cdot 10^{13}$		112,118
	O_2	293	$\sim 1.3 \cdot 10^{14}$		112,118
	He	293	$7.6 \cdot 10^{15}$		113
	Ar	293	$8.0 \cdot 10^{15}$	$\propto e^{\frac{1500}{RT}}$ or $T^{-1.8}$ (250—800° K)	113
		813	$1.70 \cdot 10^{15}$		116
		1500	$1.42 \cdot 10^{15}$	$\propto e^{\frac{1300}{RT}}$ (225 — 1850°K)	115
	H_2O	293	$1.9 \cdot 10^{17}$		113
		1350	$1.0 \cdot 10^{17}$		117
$H + OH + M \rightarrow H_2O + M$	Ar	1700	$\sim 4 \cdot 10^{15}$		69
$H + NO + M \rightarrow HNO + M$	Ar	293	$8.7 \cdot 10^{15}$	$\propto e^{\frac{700}{RT}}$ (250 — 800 °K)	113.129
	H_2	293	$1.48 \cdot 10^{16}$	$\propto e^{\frac{600}{RT}}$ (230 — 700 °K)	129
	Ne	293	$7.2 \cdot 10^{15}$		129
	He	293	$6.6 \cdot 10^{15}$		129
$O + NO + M \rightarrow NO_2 + M$	O_2,N_2,Ar	296	$2.5 \cdot 10^{16}$		90
	N_2, Ar	296	$2 \cdot 10^{16}$		84
	CO_2,N_2O	296	$4 \div 5 \cdot 10^{16}$		84
	Ar	293	$2.7 \cdot 10^{16}$	$\propto e^{\frac{1500}{RT}}$ (250 — 800 °K)	113
$NO_2 + NO_2 + M \rightarrow N_2O_4 + M$	N_2	298	$1.4 \cdot 10^{14}$		130
$Cl + NO + M \rightarrow NOCl + M$	He	293	$3.5 \cdot 10^{16}$	$e^{\frac{1100}{RT}}$ (270 — 620 °K)	131
	Ar	293	$3.9 \cdot 10^{16}$		131
	O_2	293	$3.9 \cdot 10^{16}$		131
	N_2	293	$3.5 \cdot 10^{16}$	$e^{\frac{700}{RT}}$ (270 — 620 °K)	131
	Cl_2	293	$3.4 \cdot 10^{16}$		131
	SF_6	293	$3.5 \cdot 10^{16}$	$e^{\frac{1500}{RT}}$ (270 — 620 °K)	131
$O + SO_2 + M \rightarrow SO_3 + M$	SO_3 (?)	296	$3.0 \cdot 10^{16}$		90
$O + SO + M \rightarrow SO_2 + M$	Ar	300	$3.2 \cdot 10^{17}$		132

The rates of reactions of this type (Table 5) have values which are on the whole in the same range of orders of magnitude as the rate of atomic recombination. The negative temperature coefficient in these reactions is fairly small.

3. Temperature Variation of the Rate Constant

An interesting and important feature of three-body recombination reactions, which distinguishes them from other elementary reactions, is a negative temperature coefficient of the rate constant, i.e. a negative effective activation energy $E = RT^2(d \ln k/dT)$. This fact has been established quite reliably for the vast majority of reactions of this class (see Tables 1–3, 5, and 6 and Fig. 2). Qualitatively the two possible two-stage recombination mechanisms can account for the negative activation energy. It arises because the probability of the breakdown of the intermediate complex increases with temperature faster

Table 6. Experimental temperature variation of the rate constants for the three-body recombination of iodine atoms (the constants are expressed in cm^6 $mole^{-2}$ s^{-1} and the activation energies E in cal $mole^{-1}$).

Third body M	Temp. range, °K	Empirical formula	Refs	Third body M	Temp. range, °K	Empirical formula	Refs.
Helium	293—523	$7.6\cdot10^{14}\exp(400/RT)$	123	CO_2	293—523	$6.7\cdot10^{14}\exp(1750/RT)$	123
		$4.7\cdot10^{11}\,T\exp(1400/RT)$	123			$7.4\cdot10^{11}T\exp(2400/RT)$	123
	323—543	$1.41\cdot10^{15}(298/T)^{0.60}$	122		1000—1600	$1.6\cdot10^{14}(1000/T)^{4.74}$	133
		$4.8\cdot10^{14}\exp(660/RT)$	122			$1.3\cdot10^{14}\exp(9460/RT)$	133
	1000—1600	$5.3\cdot10^{14}(1000/T)^{3.85}$	133	n-C_4H_{10}	298—493	$3.5\cdot10^{16}(298/T)^{2.16}$	127
		$1.04\cdot10^{13}\exp(7960/RT)$	133			$2.3\cdot10^{15}\exp(1650/RT)$	127
Argon	293—523	$3.1\cdot10^{14}\exp(1300/RT)$	123	CH_3I	323—543	$2.3\cdot10^{17}(298/T)^{2.24}$	122
		$3.3\cdot10^{11}T\exp(2000/RT)$	123			$1.50\cdot10^{15}\exp(2550/RT)$	122
	298—1600	$2.98\cdot10^{15}(298/T)^{1.23}$	127	C_2H_5I	293—523	$4.23\cdot10^{15}\exp(2400/RT)$	123
		$4.7\cdot10^{14}\exp(1130/RT)$	127			$4.4\cdot10^{12}T\exp(3100/RT)$	123
	1060—1860	$7.4\cdot10^{14}(1000/T)^{1.00}$	134	C_6H_6	293—523	$4.32\cdot10^{15}\exp(1700/RT)$	123
	1000—1600	$7.3\cdot10^{14}(1000/T)^{1.77}$	133			$4.4\cdot10^{12}T\exp(2400/RT)$	123
		$7.6\cdot10^{13}\exp(4560/RT)$	133		323—543	$1.0\cdot10^{17}(298/T)^{2.53}$	122
Hydrogen	323—543	$4.93\cdot10^{15}(298/T)^{1.48}$	122			$3.9\cdot10^{15}\exp(1970/RT)$	122
		$6.6\cdot10^{14}\exp(1220/RT)$	122	Toluene	293—523	$1.87\cdot10^{15}\exp(2700/RT)$	123
Nitrogen	1000—1600	$1.03\cdot10^{14}(1000/T)^{1.38}$	133			$2.0\cdot10^{12}T\exp(3400/RT)$	123
		$1.37\cdot10^{14}\exp(4240/RT)$	133		295—427	$3.4\cdot10^{14}\exp(4100/RT)$	123
	1060—1860	$7.08\cdot10^{14}(1000/T)^{1.91}$	134	Mesitylene		$3.6\cdot10^{11}T\exp(4800/RT)$	123
Oxygen	293—523	$5.1\cdot10^{14}\exp(1500/RT)$	123		293—523	$5.3\cdot10^{11}T\exp(5300/RT)$	123
		$5.3\cdot10^{11}T\exp(2200/RT$	123	I_2	298—1600	$4.5\cdot10^{10}T^{3/2}\exp(5320/RT)$	127

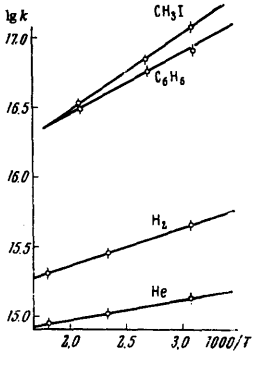

Figure 2. Temperature variation of the rate constant for the recombination of iodine atoms at moderate temperatures [122].

than the probability of the two-body collisions in both stages of the process.

The development of the experimental shock tube technique greatly extended the range of the known temperature variation of the constants. The results of the measurements of the variation of k with T are usually expressed either in terms of the exponential function $k = Ae^{-E/RT}$ ($E < 0$) or in terms of the power function $k = B/T^n$ ($n > 0$) [or $k = B'(T_0/T)^n$] (Table 6). However, more careful measurements showed [135,136] that there is a difference between the parameters E and n obtained at low (flash photolysis) and high (shock tubes) temperatures. Thus Russell [135] concluded that in the formula $k = B/T^n$ for the recombination of I and Br atoms in the presence of inert gas species at high temperatures one should use the average value $n = 1.5$, while at low temperatures the experimental data are best described by the same formula but with $n = 3$. These values are only approximate and are by no means consistent with all the experimental data. It is difficult to speak of the exact values of n or other parameters, since the results obtained at high temperatures may involve considerable errors and do not agree well with one another (see Table 6). However, there is no doubt about the actual complexity of the temperature variation, but it must now be recognised that hardly any elementary chemical reactions may be more or less satisfactorily characterised in terms of the Arrhenius function (or even less so a power function) with constant parameters over a wide range of temperatures [137] §.

The absolute values of the effective activation energies in these reactions are low and vary from zero to (minus) 5 kcal $mole^{-1}$. For example, Strong et al. [126] obtained the following activation energies in the flash photolysis of halogen–inert gas mixtures in the temperature range 25–160°C: −1.4, −2.0, and −1.2 kcal $mole^{-1}$ respectively for the recombination of I atoms in argon, Br atoms in argon, and Br atoms in molecular oxygen. Analysis of the experimental data carried out by Bunker and Davidson [17] showed that the negative temperature coefficient is higher for the gases which are more effective at low temperatures Hence here again there is a correlation between E and the boiling points, critical temperatures, etc. This conclusion is not confirmed by the earlier results of Russell and Simons [80], which are less reliable as regards the temperature variation, since these workers did not allow for the high effectiveness of I_2 as a third body (see p. 597).

According to Husain and Pritchard [138], the variable negative activation energy can be readily interpreted in terms of the ET mechanism if it is assumed that the collision with a third particle leads to the deactivation of the already formed excited ("latent") molecule only when the energy of the relative motion of the recombining particles lies in the range between two critical values ϵ_0 and ϵ_1 (above ϵ_1 there is no deactivation). Then the recombination rate constant should be

$$k = z[\exp(-\epsilon_0/RT) - \exp(-\epsilon_1/RT)] \quad (4)$$

Differentiation of this expression shows that k will decrease with increasing temperature if $\epsilon_0 < RT$ and $\epsilon_1 - \epsilon_0 \ll RT$. It is reasonable to put $\epsilon_0 = 0$; then if one adopts, for example, $\epsilon_1 = 0.1$ and 0.5, we obtain for the recombination

§In the present case one of the possible reasons for this is also the fact that the relative contributions of the ET and RMC mechanisms may vary with temperature.

reaction respectively $E_{300-400} = -0.68$ and -0.51 kcal mole^{-1} and $E_{1000-2000} = -2.72$ and -2.53 kcal mole^{-1} (the subscripts to E denote the temperature ranges). The numerical values thus obtained are extremely plausible, despite the simplified nature of the model: they give a temperature coefficient of the right order of magnitude, the absolute value of which increases at high temperatures in agreement with the results of the majority of the experiments.

4. Energy Distribution Among Recombination Products. Repeated Dissociation and Its Effect on the Temperature Variation of the Rate Constant

In the light of the latest experimental and theoretical data for energy transfer processes, it is fairly reliably known that the conversion of vibrational energy into translational energy, i.e. a process of the type

$$A_2'(v = n) + M \rightarrow A_2'(v = n - 1) + M + Q$$

(a single prime denotes a vibrationally excited molecule) is extremely difficult and is much slower than the transition from one vibrational level to another. The effective deactivation of A_2' requires a very large number of thermal collisions, i.e. it takes place with a very long relaxation time. Therefore it is logical to expect that an elementary exothermic reaction leads to the formation of vibrationally excited molecules, which are then gradually deactivated by collisions with the inert gas molecules. This is confirmed by a series of experiments with elementary bimolecular and termolecular reactions of the type $A + BC \rightarrow AB' + C$ and $A + B + C \rightarrow AB' + C$. For example, according to data of McGrath and Norrish [139], the reaction of atomic oxygen with ozone takes place as follows: $O + O_3 \rightarrow O_2'(v = 17) + O_2$. Cashion and Polanyi [140-143] and also Charters and Polanyi [144], who studied the reaction $H + Cl_2 \rightarrow HCl' + Cl$, arrived at analogous conclusions: the energy distribution among the products formed proved to be displaced from the Boltzmann distribution towards higher vibrational levels. Among termolecular reactions, we may quote as an example the recombination of nitrogen atoms, for which it has been shown [141,145,146], that the N_2' molecule forms at the level with $v = 4$. Villermaux [147] investigated from this standpoint the recombination of hydrogen atoms by a thermal-kinetic method, which is based on the following simple idea: if the energy evolved in the recombination is instantly transferred to translational-rotational degrees of freedom, then the rate of evolution of heat should be equal to the rate of disappearance of atoms (known from other experiments); otherwise the rates are different. The experiments in fact showed that the latter is the case.

Polanyi [148] suggested that, since the recombination product is a vibrationally excited molecule A_2, its repeated dissociation (redissociation) at higher vibrational levels may play an important role. Polanyi made an approximate calculation of the probability of repeated dissociation at 300° and 600°K, assuming that the distance between adjacent vibrational levels close to the dissociation threshold is constant and that there exists a characteristic probability of the change in the quantum number by the same amount, which is independent of temperature. Calculation showed that the total probability of redissociation at all levels in the second and third collisions is 0.175 at 300°K and 0.29 at 600°K. This corresponds to a decrease with increasing temperature in the component of the recombination which definitely contributes to the negative temperature variation of the rate constant. Polanyi obtained an effective activation energy $E = -0.85$ kcal mole^{-1} in the range 300–600°K. The value thus predicted is smaller by a factor of 2–3 than the experimental activation energy, but it may be that, as a result of the above assumptions, it constitutes a lower limit.

Repeated dissociation is only one of the factors contributing to the negative temperature variation, but it is evident that, when this phenomenon is correctly taken into account, complete understanding of the experimental values may be greatly facilitated.

5. Deviations from the Termolecular Law. Anomalously High Efficiencies of Certain Third Bodies

The first experiments on the recombination of atoms showed that the termolecular law holds exactly. However, in 1954–1955 Christie and coworkers [121,149], having revised the results of their earlier study [120] on the recombination of iodine atoms in the presence of noble gas atoms by experiments over a wider range of conditions, observed deviations from the simple relation $d[I_2]/dt = k_M[I]^2[M]$ when the concentration ratio $[I_2]/[M]$ was varied (Fig. 3).

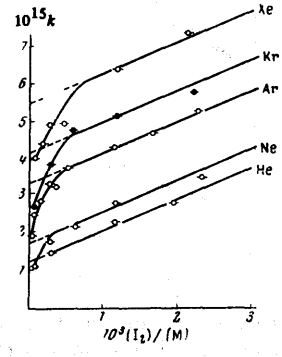

Figure 3. Deviations from the termolecular law in the recombination of iodine atoms [150].

The experimental results showed that the effective rate constant for the formation of molecules is a linear function of the ratio $[I_2]/[M]$ over a wide range of the latter, the relation showing a sharp variation at low values of $[I_2]/[M]$.

In the first series of experiments [120] the variation of the rate constant with $[I_2]/[M]$ was apparently masked by a "thermal effect". Since the recombination process is exothermic, the gas mixture is heated in the course of this process. The exact value of the heat evolved ΔQ depends on the average wavelength of the light absorbed; if we adopt $\Delta Q = 60$ kcal per mole of iodine as the maximum value and assume that the process is adiabatic, we can estimate the increase of temperature: $\Delta T = 3 \times 10^4 \Delta[I]/c_V[M]$, where $\Delta[I]$ is the change in the concentration of free iodine atoms and c_V the heat capacity of the third body M which is present in excess. For a monatomic gas, $\Delta T = 10^4\Delta[I]/[M]$ and, when $[M] = 100$ mmHg and $[I]_0 = 0.1$ mmHg, we obtain $\Delta T = 10$ deg after complete recombination. The direct effect of this temperature rise is hardly significant, but the temperature gradient thus

produced may be important [80]. This thermal effect, which increases with $[I_2]/[M]$, is revealed by a decrease of the observed rate constant during the recombination, compensating thereby the true increase of the constant as $[I_2]/[M]$ is raised. To explain the last finding, the rapid reaction $I + I + I_2 \rightarrow I_2' + I_2$ was postulated. When this and the process $I + I + M \rightarrow I_2 + M$ are taken into account, the kinetic law changes:

$$\frac{d[I_2]}{dt} = k_M[I]^2[M] + k_{I_2}[I_2][I]^2 = k_{init}[I]^2[M] , \quad (5)$$

$$k_{init} = k_M + k_{I_2}[I_2]/[M] , \quad (6)$$

where k_M and k_{I_2} are the true termolecular constants for the third bodies M and I_2 respectively and k_{init} is the effective rate constant determined experimentally in the initial stage of the recombination. Eqn. (6) shows that this constant does indeed vary linearly with $[I_2]/[M]$ and the fact that the straight lines in Fig. 3 are parallel confirms satisfactorily that the slope is related solely to the effectiveness of the I_2 molecule as third body and is independent of the nature of the inert gas M. The slope of the straight lines in Fig. 3 corresponds to $k_{I_2} \simeq 8.5 \times 10^{17}$ cm^6 mole^{-2} s^{-1} at room temperature, which is approximately 260 times higher than k_{Ar} (by a factor of 650 according to the data of Bunker and Davidson [127]). Evidently such high effectiveness of I_2 cannot be explained solely by an increase of the kinetic collision cross-section. However, as early as 1932, Rollefson and Eyring [151] predicted theoretically the possibility of the existence of relatively stable triatomic halogen molecules. The hypothesis of the formation of an I_3 molecule of this kind in the recombination of iodine atoms explains satisfactorily the anomalously high effectiveness of I_2 as the third body M. According to Semenov's estimate [108], the above experimental results correspond to $\Delta E \simeq -6$ kcal mole^{-1} as the energy of formation of I_3 in the reaction $I + I_2 \rightleftharpoons I_3$; Bunker and Davidson [17] quote for the same reaction $\Delta H^\circ = -5.3$ kcal mole^{-1} and $\Delta S^\circ = -20$ e.u.¶.

The rate constant k_{I_2} falls with temperature much faster than those for less effective third bodies (Table 6): at 1300°K the ratio k_{I_2}/k_{Ar} no longer exceeds 30. [133] This fact is in good agreement with the general tendency towards an increase of the negative temperature coefficient with increase of the effectiveness of recombination described in Section II, subsection 3.

For the recombination of Br atoms, it has also been reliably established that the species $M = Br_2$ is distinguished by enhanced effectiveness, although not to the same extent (Tables 7 and 8); an even smaller relative effect is observed [45,152] for $M = Cl_2$ in the reaction $Cl + Cl + M \rightarrow$ product and, finally, there exist only qualitative data indicating that in the recombination of F atoms molecular fluorine is somewhat more effective than argon [153].

The deviation of the rate constant from Eqn. (6) at low values of $[I_2]/[M]$ (Fig. 3), observed by Christie and coworkers [121,149], probably demonstrated for the first time a breakdown of the equilibrium distribution in the recombination of atoms. Generalising the various experimental data, Christie [150] concluded that the deviations from linearity may be attributed to the retardation of the vibrational deactivation of the excited molecule I_2' (formed in the recombination) as the concentration of I_2 diminishes. Although it is known that iodine molecules are initially formed at high vibrational levels, it is nevertheless always postulated that, of the two possible processes

$$I + I + M \rightarrow I_2' + M , \quad (a)$$

$$I_2' + M \rightarrow I_2 + M , \quad (b)$$

the rate-determining stage is the recombination (a), i.e. it is assumed that process (b) is fairly rapid. This assumption is justified if various gases have the same effectiveness in the two processes. If, however, molecular iodine is much more effective (by a factor of 10^4 and more) than an inert gas in the deactivation of I_2', then process (b) proceeds mainly in the following way even at very low values of $[I_2]/[M]$: $I_2' + I_2 > 2I_2$ ($v < 3$); when the contribution of $M = I_2$ to the overall rate of recombination (a) is negligibly small, then process (b) may become the rate-determining stage under the condition $k_b[I_2'][I_2] < k_M[I_2][M]$. Thus a deviation from linearity occurs when $([I_2]/[M])_{dev} = k_M[I_2]/k_b[I_2']$ and, under the initial experimental conditions, $([I_2]/[M])_{dev}$ should be proportional to k_M, as found experimentally (Fig. 3).

Table 7. Rate constants for the recombination of bromine and chlorine atoms close to room temperature.

Third body M	$10^{-15}k$, cm^6 mole^{-2} s^{-1}	Refs.	Third body M	$10^{-15}k$, cm^6 mole^{-2} s^{-1}	Refs.
$Br + Br + M \rightarrow Br_2 + M$			$Cl + Cl + M \rightarrow Cl_2 + M$		
Ar	2.4	77	He	3.0	152
	3.73	128	Ar	4.0	152
	2.7	154		4.25	45,46
	2.0	155	Cl_2	27	152
Br_2	49	154		0.3**	157
	48*	156		20.4	45,46
	260	155	O_2	7.9***	158
Cl_2	15*	156			
CO_2	9.8	77			
	7.8	128			
O_2	5.8	77			
	7.9	128			
H_2	4.0	77			
He	1.4	77			
N_2	4.5	77			
CH_4	6.5	77			

*The results quoted were obtained from a study of the photochemical reaction $Br_2 + Cl_2 \rightarrow$ product by comparing the effectiveness of Br_2 and Cl_2 with that of CO_2, using for the latter the result of Rabinowitch and Wood [77] (the direct determination was difficult in view of the heterogeneity of the thermal reaction).

**This result deviates markedly from the data of other workers; possibly, the method used here may yield relatively unreliable results in the presence of excited species [45].

***Measured at 229°K.

However, Nikitin [164,165] believes that for the recombination reactions under conditions of flash photolysis this interpretation is incorrect; according to his estimate, in this case (recombination of iodine) the disequilibrium arises due to the retardation of the transition between the excited and ground electronic states of I_2. In the formation of the system $I_2'-I_2$ there arise electronic levels strongly differing from those for two isolated I_2 molecules

¶Here the situation differs from that which obtains in the recombination of H atoms (see p. 597), since the diatomic product molecule is the chemically active third body. It would be interesting to carry out experiments designed to investigate the effectiveness of free halogen atoms as the third body M.

and there is a high probability of non-adiabatic transitions in the region where the energy levels of the complex I_2'–I_2 come very close together. In the interaction of I_2 with an inert gas atom one cannot expect a pronounced change in the position of the electronic levels; this accounts for the large difference between the effectiveness of the relaxation of I_2' on collision with M = I_2 and inert gas atoms.

Table 8. Rate constants for the recombination of halogen atoms at high temperatures.

Third body, M	T, °K	$10^{-15}k$, cm^6 mole^{-2} s^{-1}	Refs.	Third body M	T, °K	$10^{-15}k$, cm^6 mole^{-2} s^{-1}	Refs.
	I + I + M → I_2 + M				Br + Br + M → Br_2 + M		
He	1300	0.25	133	He	1700	0.32	161
Ar	1300	0.45	133	Ar	1770	0.29	162
	1460	0.36	134		1600	0.33	81
O_2	1300	0.53	133		1700	0.40	161
N_2	1300	0.71	133	HBr	1600	0.39	163
	1460	0.35	134	Br_2	1600	2.6	81
I_2	1300	13.5	133		1600	3	163
					1770	0.73	162
	Cl + Cl + M → Cl_2 + M				F + F + M → F_2 + M		
Ar	1600	2.5	159	Ar	1400	0.007	153
	2100	0.17	160				

The constants for the midpoint of the temperature range of the measurements are quoted in the table.

It is noteworthy that the very high effectiveness is observed also in other cases where there is a possibility of a chemical bond: for example, with M = NO in the recombination reactions of halogen atoms (Table 4).

6. Effect of the Third Body in the Recombination of Alkyl Radicals

Since alkyl radicals are fairly complex species, in their recombination there is a relatively high probability of their stabilisation as a result of internal energy redistribution; nevertheless at low pressures the role of deactivation in collisions with a third body increases, leading to significant deviations towards a third-order process. The kinetic mechanism of such reactions is usually expressed in terms of the energy transfer mechanism (ET); then the general equations show that the effect of the third body begins to operate at higher pressures the lower its deactivating capacity. Furthermore, this effect becomes more pronounced with increase in temperature due to the decreased life-time of the complex R_2^*, which demonstrates the significant role which it may play in high-temperature pyrolytic processes.

Numerous experiments [166–174] have now yielded a fairly large number of quantitative data for the simplest process of this type—the recombination of methyl radicals:

$$CH_3 + CH_3 \underset{k_B}{\overset{k_A}{\rightleftharpoons}} C_2H_6^*,$$

$$C_2H_6^* + M \xrightarrow{k_C} C_2H_6 + M,$$

whence the rate of accumulation of ethane is:

$$\frac{d[C_2H_6]}{dt} = \frac{k_A k_C}{k_B + k_C[M]}[CH_3]^2[M]. \quad (7)$$

Under the condition $k_C[M] \ll k_B$, a third-order process is realised:

$$\frac{d[C_2H_6]}{dt} = \frac{k_A k_C}{k_B}[CH_3]^2[M] = k_{eff}[CH_3]^2[M] \quad (8)$$

Ingold and Lossing [166] measured mass-spectrometrically the rate of recombination of methyl radicals produced by the thermal decomposition of dimethylmercury and found that the rate has a negative temperature coefficient, without observing at the same time deviations from a second-order process as the helium pressure changed from 18.5 to 4.8 mmHg; this contradicts both the observed negative temperature coefficient and the low deactivating capacity expected for helium. Indeed, as was to be expected, repetition of the observations [167] revealed a linear variation with [He]. Although the negative temperature coefficient of the rate (according to Ingold and Lossing, $E = -2.2$ kcal mole^{-1}) is satisfactorily consistent with the known general properties of three-body recombination reactions, this phenomenon in the recombination of CH_3 radicals can be explained in another way not involving a third-order process [175].

The effect of the third body in this reaction was studied by Kistiakowsky and Roberts [168] and almost simultaneously by Dodd and Steacie [169] in experiments on the photolysis of acetone. These experiments showed that at temperatures in the range 150–250°C the deviations become significant at pressures of about 10 mmHg, which agrees well with the theoretical prediction of Marcus [172] concerning the existence of a transition region near 5 mmHg. According to Dodd and Steacie [169], the rate of spontaneous dissociation of $C_2H_6^*$ at 250°C is not greater than 6×10^7 s^{-1} (lifetime $\geq 1.6 \times 10^{-8}$ s) and increases with increasing temperature, and for the effectiveness of various third bodies in the deactivation of $C_2H_6^*$ these workers found the following values (relative to acetone): Ar(< 0.03), CO_2 (0.03), C_4F_{10} (0.2), $CF_3.C_6F_{11}$ (0.3), C_6H_6 (1.0), and acetone (1.0) at a temperature near 250°C. The absolute values of the effective third-order rate constants are then much higher than for the recombination of atoms.

Among the later investigations, the experiments of Toby and Weiss [173] on the photolysis of azomethane yielded important results. Azomethane proved to be a deactivating agent less effective by a factor of approximately three than acetone, which made it possible to extend the range of investigation of the effect of the third body to higher pressures. Carbon dioxide and sulphur hexafluoride were also investigated as third bodies, and their effectiveness in relation to azomethane proved to be 0.04 and 0.24 respectively.

Numerous experimental data on the recombination of CH_3 radicals in the transition region were analysed by Kondrat'ev [176]. This analysis led to the most reliable values of the kinetic characteristics of the process.

When the reactions of ethyl and more complex radicals are examined, the situation becomes somewhat more complicated. Qualitatively it is clear that the effect of the third body can operate here at even lower pressures; furthermore, the recombination is accompanied by disproportionation reactions, which complicate the composition of the products.

In experiments on the photolysis of diethylmercury, Bradley et al. [177] investigated the kinetics of the interaction of ethyl radicals and the composition of the products; the effect of the third body becomes clearly apparent at low pressures of M = Ne. However, the authors' interpretation of the experimental data in this region is incompatible

with the energy transfer mechanism. The authors' treatment is based on the postulate that the three-body recombination of C_2H_5 radicals is an independent reaction which takes place simultaneously with bimolecular recombination and disproportionation. Then the composition of the products is a linear function of pressure of the following form:

$$\frac{[\text{butane}]}{[\text{ethane}]} = \frac{1}{R} + \frac{k_{tr}}{k_r + k_d} \cdot \frac{1+R}{R}[M]. \quad (9)$$

where k_r and k_d are the rate constants for the bimolecular recombination and disproportionation reactions, k_{tr} is the three-body recombination rate constant, and $R = k_d/k_r$, which is equal to the ratio [ethane]/[butane] in the absence of the termolecular process. Extrapolation using Eqn. (9) to [M] = 0 yields R and then

$$\frac{k_{tr}}{k_r + k_d}.$$

However, the initial postulate of the separate occurrence of bimolecular and termolecular recombination of radicals gives rise to objections. It leads to the conclusion that at fairly high pressures three-body recombination will completely "suppress" bimolecular recombination, while experiments in fact show that the third-order law is fulfilled only at extremely low pressures. It is most likely that, as in simpler cases, these reactions are part of the same process, the order of which may change with pressure:

$$C_5H_5 + C_2H_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_4H_{10}^* ,$$

$$C_4H_{10}^* + M \xrightarrow{k_2} C_4H_{10} + M ,$$

$$C_2H_5 + C_2H_5 \xrightarrow{k_3} C_2H_6 + C_2H_4$$

and the ratio of the product concentrations can also be expressed in terms of the relation

$$\frac{[\text{butane}]}{[\text{ethane}]} = \frac{k_1 k_2}{k_3} \frac{[M]}{k_{-1} + k_2[M]} ,$$

which is probably the true one. This relation is close to linearity only when $[M] \ll k_{-1}/k_2$; on the other hand, extrapolation to [M] = 0 when experimental points relatively far from this value are available may lead to considerable errors. When $[M] \to 0$, we have [butane]/[ethane] $\to k_1k_2[M]/k_{-1}k_3 \to 0$ provided that all the important elementary stages are incorporated in the mechanism quoted above.

It is remarkable that at very much higher pressures, when the ET mechanism gives rise to a second-order process, there is a possibility in principle of the simultaneous occurrence of three-body recombination, but solely by an RMC mechanism, i.e. with a different rate constant. In other words, we are dealing with the possible occurrence of a second transition (in the sense of a change in reaction order) pressure range. Unfortunately so far there are no data on the kinetics of radical recombination under conditions where this effect might be expected to occur.

There is extremely little information about the role of third bodies in the reactions of more complex radicals. However, theoretically for each case of this kind it is possible to predict a pressure range where the kinetic order of the recombination process should change [197].

III. INTERPRETATION OF EXPERIMENTAL DATA

Many theoretical papers on the problem of the three-body recombination of atoms have now been published. These studies are concerned both with the discussion of the general dynamics of the interaction of three atoms in the course of recombination and with the analysis of the possible two-stage process mechanisms from the standpoint of the classical and quantum mechanics and statistical physics. Modern theories of atomic recombination have been reviewed [165,203]. Here we shall consider only the possibility of the interpretation of the kinetics of three-body recombination on the basis of the simplest theoretical concepts—the kinetic collision theory and the activated complex method.

1. The Collision Theory

As for other elementary gas-phase reactions, the first attempt at the interpretation of the experimental data on three-body recombination involved the use of the Arrhenius formula (1). Before the discovery and systematic investigation of the negative temperature dependence, it was usually assumed that $E = 0$ in this formula, in the belief that the addition of free atoms or more complex paramagnetic species with unpaired spins does not require activation energy. The problem thus reduced to the calculation of the pre-exponential factor in formula (1), which is identifiable with the number of triple collisions z (possibly with an accuracy to within the steric factor $s \leq 1$, so that $A = sz$). According to Bodenstein's earliest estimate [2],

$$\frac{\tau_{12}}{\tau_\lambda} \simeq \frac{d}{\lambda} , \quad (10)$$

where τ_{12} is the duration of the ordinary (two-body) collision, τ_λ the time taken for the particle to traverse its free path, λ the mean free path, and d the diameter of the molecule. However, the fraction of the total time during which the molecule formed collides is approximately equal to the ratio of the number of three-body collisions to the total number of collisions. At atmospheric pressure it amounts to 1/1000; nevertheless Rabinowitch's experiments [75-79] showed that three-body recombination takes place more effectively.

Tolman [3] based his interpretation on the calculation of the average lifetime of the pair formed in the two-body collision when the particles approach one another to a distance not greater than δ. Then the number of elastic collisions of all the particles in an ideal gas can be calculated from Eqn. (2) if the steric factors are neglected.

Other workers proposed different versions of the calculation of the number of three-body collisions, differing mainly in the model adopted: for example, according to Herzfeld [11], the same formula is obtained but δ is treated as the average diameter of the colliding particles; according to Syrkin [178], a three-body collision occurs when all the particles are within a sphere of radius r and the formula differs somewhat from Eqn. (2). Thus all the formulae contain an undetermined parameter which characterises in one way or another the effective region of operation of intermolecular forces. In Tolman's equation (2) this parameter (δ) is defined as the maximum distance between particles 1 and 2 and 1 and 3.

It should be noted that, in the recombination of atoms in collisions with not unduly effective inert gas species even the above simplest formula gives rise to fairly good agreement with the experimental rate constants when a reasonable value of δ is chosen [108,179]. This applies of course only to the absolute value of the constant and agreement is observed only close to room temperature.

Over a wider range, Eqn. (2) is naturally inconsistent with experiment, since it does not constitute a general expression for the rate constant; this is evident if only from the fact that it predicts an increase of the rate constant with temperature as $\sqrt{T}$†. Furthermore, the interpretation of the higher effectiveness of certain third bodies (for example, benzene or a number of other hydrocarbons) on the basis of formula (2) alone would require anomalously high kinetic diameters [180]. Rabinowitch [15] gave a detailed interpretation of his own experiments and those which he carried out together with Wood [76-79] on the recombination of atoms (A + A → product), using the simple collision theory and thus avoiding the difficulties associated with the indeterminacy of the kinetic diameter of the excited molecule $d_{A_2^*}$ in Steiner's treatment [6]. When the two possible recombination mechanisms were taken into account, i.e. (A + A) + M → product and (A + M) + A → product, the total number of three-body collisions leading to recombination was obtained:

$$z = 4\sqrt{2}\,\pi d_{AM}^2 d_{AA}^2 \frac{RT}{m_A}\sqrt{\frac{m_A + m_M}{m_M}}\,N_A^2 N_M (2\tau_{AA} + \tau_{AM})\beta \quad , \quad (11)$$

where τ_{AA} and τ_{AM} are the lifetimes of the corresponding complexes and β is the effectiveness (the "steric factor")‡. Assuming that the experimental rate constant is equal to the number of collisions determined in this way, Rabinowitch calculated from the experimental data the value of $(2\tau_{AA} + \tau_{AM})\beta$. In Table 9 these values are quoted together with later results for A = I; they are somewhat too high, but in general they express correctly the tendency for the given quantity to increase on going to more complex third bodies.

This simple analysis of the recombination process in three-body collisions clearly shows that the high effectiveness of the latter (relative to Bodenstein's initial estimate) depends not so much on the diameter as on the large difference between the distance over which the interaction begins and the distance of closest approach of the particles. Rabinowitch's explanation of the much higher values of τ calculated from experiments with benzene and pentanes, based on "sticky" collisions between the atom and M, is more likely than the possibility of anomalously large cross-sections of the vibrational deactivation of A_2^* by these molecules (ET mechanism).

In the more general form, when account is taken of all possible mechanisms of the termolecular reaction A + B + C → product and the steady-state concentrations of the binary complexes AB, BC, and CA are calculated initially, the model of an elastic spherical collision leads to the following formula for the experimental rate constant [181]:

$$k = s_C z_{AB.C} z_{AB} \tau_{AB} e^{-E_C/RT} + s_A z_{BC.A} z_{BC} \tau_{BC} e^{-E_A/RT} + s_B z_{CA.B} z_{CA} \tau_{CA} e^{-E_B/RT} \quad , \quad (12)$$

Here z_{AB}, $z_{AB.C}$, etc. are the numbers of two-body collisions between the initial particles and between the binary complex and the third particle, τ_{ab} etc. are the lifetimes of the corresponding binary complexes, which are equal to the reciprocals of their decomposition rate constants, and s are steric factors. Incidentally, even this simple treatment shows that, in general, with a rigid model the steric factors for trimolecular reactions should be lower than for bimolecular reactions [182]. Indeed, Eqn. (12) shows that $s_C = s_{AB} s_{AB.C}$ if AB etc. are species actually produced in the process, the formation of which is characterised by a particular steric factor in each case.

Table 9. Experimental values of $10^{13}(2\tau_{AA} + \tau_{AM})\beta$ (seconds).

A	Third body M										Refs.
	He	H_2	Ar	N_2	O_2	CH_4	CO_2	C_5H_{12}	neo-C_5H_{12}	C_6H_6	
Br	0.64	1.2	2.0	3.2	4.5	3.4	6.9				15
I	1.2	1.7	5.0	7.3	12.5	9.6	20.0			84	15
I			3.0					36	32		125

Then $s_{AB.C}$ is the steric factor of the AB + C collision under the condition that AB has in fact formed, i.e. it expresses the conventional probability of the configuration AB...C. Since, from their nature, both s_{AB} and $s_{AB.C}$ are less than unity, it is clear that s_C is less than s_{AB}. If the effective activation energies E_A, E_B, and E_C are low, the steric factors, which are themselves functions of temperature, may have a marked influence on the temperature variation of the rate constant [182,183].

The explanation of the properties of three-body recombinations based on the simple kinetic model involving collisions of structureless particles is of course primitive and constitutes only a first approximation. However, in many simple systems it leads to reliable estimates and helps in extracting useful information from experimental data.

However, we may mention here one difficulty which is common to all three-body recombination theories and which has still not been completely overcome–the problem of the so called "statistical factor". Let us consider as an example the thoroughly investigated recombination of iodine atoms. It is known [184] that two I atoms in the ground electronic state $^2P_{3/2}$ may interact with formation of molecules in the states $^1\Sigma_g^+$, $^1\Pi_u$, and $^3\Pi_{2u,1u}$ whose potential energy curves have minima. The assumption that recombination can give rise only to the ground molecular state $^1\Sigma$ would imply the introduction of a statistical factor of 1/16 in the expression for the rate constant; allowance for other electronic states increases this factor. According to Rabinowitch [15], the interaction of recombining atoms begins at very long distances, for which the energy differences between the curves are very small, so that the perturbing effect of the third body may ultimately lead to a transition from the unstable to a stable curve and then in general any collision of two atoms in the presence of an approaching third particle may be effective for stabilisation and all statistical limitations should be removed. Probably this is an overstatement, but so far there exists no single view concerning this problem and various workers make different allowances for the statistical effect.

†Strictly speaking in a real gas the temperature variation of z according to Eqn. (2) is less pronounced because the diameters vary in accordance with Sutherland's formula:

$$d^2 = d_\infty^2\left(1 + \frac{C}{T}\right) \quad .$$

‡In a more general derivation account must of course be taken of the fact that $\beta \neq$ const for the two types of collisions, i.e. the corresponding factor should be replaced by $2\tau_{AA}\beta_1 + \tau_{AM}\beta_2$. The experiments of Christie et al. [120] showed that in the recombination of iodine $\beta_1 < \beta_2$ (the best values are $\beta_1 = 0.04$ and $\beta_2 = 0.7$).

2. Three-body Recombination of Particles and the Theory of Equilibrium Reaction Rates. Application of the Surface Potential Function. Certain Modifications of the Collision Theory and Analysis of the Trajectories

The determination of the rate constant for an elementary chemical process by methods of the transition state theory (TST) requires detailed information about the interaction between the reacting particles. This interaction is usually represented by a potential energy surface [185].

Both the general methods of construction and the properties of potential surfaces are well known as are the solutions for many specific problems within the framework of TST; [9,186] therefore we shall confine ourselves here to certain general features characteristic of the class of reactions with which we are dealing.

It has been shown [9] that in many cases the state of a three-atom system having minimum potential energy is colinear—all three atoms are located on a single straight line (we may note that in systems with an inert third atom there is also a possibility that other configurations are effective in stabilising the molecule formed). For a colinear system, the construction of a potential energy surface is particularly convenient, and the process may be readily interpreted. Fig. 4 presents such surfaces, describing the combination of atoms A + B + C → AB + C in two cases: when the atoms B and C interact to a considerable degree and when they almost do not interact at all.

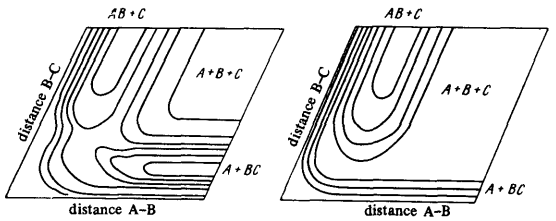

Figure 4. Potential energy surfaces for three-body recombination reactions: *a*) atoms B and C interact chemically; *b*) atoms B and C scarcely interact.

The flat "plateau" in the upper right-hand corner corresponds to the completely dissociated state; if the two atoms form a bond, then a deep "valley" is obtained in the figure, which is parallel to the corresponding coordinate axis when the distance from the third body is very large. Let us consider the first case. If the representative point rolls from the plateau straight into the AB + C valley, then transverse motions, i.e. vibrations, can return it to the plateau and the reaction will not occur. A stable molecule is formed only when the point rolls into the AB + C valley at an appropriate angle, i.e. with a sufficient store of translational and vibrational energy, and crosses the ridge into the product valley; then the translational energy is transformed into vibrational energy. If B and C interact fairly strongly, then the valley parallel to the abscissa axis is deeper and the ridge separating it from the product valley is relatively low, which leads to high effectiveness of C as the third body. It is precisely this case that is realised, for example, in the recombination H + H + H → product (cf. Section II, subsection 1). On the other hand, if the third atom is inert (Fig. 4*b*), the A + BC valley is shallow, the plateau is very wide, and for the reaction to occur the point must reach the region with curved equipotential lines (pathway 1): otherwise the point will be "reflected" from the lower edge of the valley (pathway 2). This imposes more severe limitations on the angle at which the point would leave the plateau, significantly reducing thereby the probability of the reaction. Gershinowitz [187] constructed the exact potential energy surface for the particular case of the H + H + He collision; the probability of the reaction was indeed found to be relatively low. A similar study was also made by Rabinowitch [15].

Eyring et al. [54] calculated the rate constants for the recombination of three hydrogen atoms by TST methods:

$$k = \gamma \frac{g^{\neq}}{g_i} \cdot \frac{[2\pi(m_1+m_2+m_3)\,kTh^{-2}]^{3/2}\prod_{j=1}^{3}(1-e^{-h\nu_j/kT})^{-1}}{(2\pi m_1 kTh^{-2})^{3/2}(2\pi m_2 kTh^{-2})^{3/2}(2\pi m_3 kTh^{-2})^{3/2}} \cdot \frac{8\pi^2 \mathcal{J}^{\neq} kT}{h^2 \sigma^{\neq}} H\bar{v} \cdot \quad (13)$$

In this formula the superscript ≠ denotes quantities referring to the activated complex, γ is the transmission coefficient, g the electronic degeneracy, $\mathcal{J}^{\neq}$ the moment of inertia, ν_j the vibration frequency, $\sigma^{\neq}$ the symmetry number, and $\bar{v} = (kT/2\pi\mu)^{1/2}$ the average velocity with which the point intersects the symmetry axis of the corresponding potential energy surface [9,186]. The factor H constitutes the vibrational component of the partition function of the activated complex, which is responsible for the energy distribution in the latter leading to reaction. Eqn. (13) follows from the more general formula derivable from TST for the rate constant of any trimolecular reaction [8]:

$$k = \gamma \frac{kT}{h} \frac{Q_{(A\ldots B\ldots C)^{\neq}}}{Q_A Q_B Q_C} e^{-E_0/RT} \quad (14)$$

where $Q_{(A\ldots B\ldots C)^{\neq}}$, Q_A, Q_B, and Q_C are the partition functions of the activated complex and the total partition functions of the initial species and E_0 is the zero-point activation energy.

Eyring et al. [54] constructed the potential energy surface on the assumption that in the H–H interaction the Coulombic integral amounts to 14% of the total bond energy § and is independent of the distance. This assumption is permissible, since in calculations of this kind only a relatively small region of the configurational space near the activated state is important (incidentally, this is why analogous assumptions are possible also for certain other parameters). Several additional assumptions concerning the geometry and frequencies of the activated complex permitted the complete calculation of the rate constant, which proved to be 3.1×10^{15}. Eyring et al. [54] also considered the possibility of a different configuration of the activated H...H...H complex—in the form of an equilateral triangle. Then the rate of formation of H_2 proved to be less; nevertheless the correction for the possible non-linear configuration may bring still closer together the theoretical and experimental values.

The application of TST methods makes it particularly convenient to consider the problem of the pre-exponential factor associated with the rate constant as expressed by the Arrhenius formula (1) or obtained directly from formula (14). The point is that, for a wide class of reactions with low activation energies, it is in fact the variation of the pre-exponential factor (or more correctly the steric factor) that is responsible for the temperature variation of the rate constant at fairly high temperatures. This effect

§The possibility of making such estimates has already been discussed [108] (Appendix II).

of the pre-exponential factor may be very large. For example [182], in the general case of a trimolecular reaction (between complex species) the pre-exponential factor in Eqn. (14) varies with temperature as $\varphi(T)/T^5$, where $\varphi(T)$ denotes the contribution of the vibrational partition functions; thus if the vibration frequencies are high, the pre-exponential factor decreases with temperature in proportion to $1/T^5$.

The method developed by Stepukhovich and co-workers [188-192] for bimolecular reactions permits the calculation of the pre-exponential and steric factors provided that the geometry and the frequencies of the activated complexes are known (or postulated), without the necessity of knowing the activation energy. This method is applicable also to trimolecular reactions. Since the number of three-body collisions varies with temperature as $\sqrt{T}$, one can write according to Eqn. (2).

$$E_{exp} = E_0 + \frac{1}{2}RT \ , \qquad (15)$$

$$E_{exp} = E_0 + RT^2 \frac{d \ln A^{\neq}}{dT} \ , \qquad (16)$$

where $A^{\neq}$ is the pre-exponential factor in Eqn. (14); then comparison of this equation with the formula $k = sze^{-E/RT}$ yields the following expression for the steric factor:

$$s = \gamma \frac{kT}{h} \frac{1}{z} \frac{Q_{(A\ldots B\ldots C)^{\neq}}}{Q_A Q_B Q_C} \exp\left\{\frac{1}{2} + T\frac{d}{dT} \ln \frac{Q_{(A\ldots B\ldots C)^{\neq}}}{Q_A Q_B Q_C}\right\} \ . \qquad (17)$$

Stepukhovich and Umanskii [182] applied this method and Eqn. (17) in the approximate calculation of pre-exponential and steric factors and the rate constants for the three-body recombination of halogen atoms in collisions with inert gas atoms on the basis of the hypothesis of a triangular configuration of the activated complex. It was assumed that the bond between the halogen atom and the inert gas atom is of the van der Waals type and that the energy of this bond is approximated by the 12-6 Lennard-Jones potential [193,194]:

$$\varepsilon(r) = 4\varepsilon_0 \left[\left(\frac{\sigma_0}{r}\right)^{12} - \left(\frac{\sigma_0}{r}\right)^{6}\right] \ , \qquad (18)$$

where ϵ_0 is the depth of the potential well and σ_0 the distance over which the potential becomes zero (attraction and repulsion forces are equal). In order to estimate σ_0 and ϵ_0 for halogen atoms, values taken from the viscosity data for the nearest inert gas were used, the interaction parameters being calculated according to the following rules [193]:

$$\sigma_0^{12} = \frac{1}{2}(\sigma_0^1 + \sigma_0^2); \ \varepsilon_0^{12} = (\varepsilon_0^1 \varepsilon_0^2)^{\frac{1}{2}}. \qquad (19)$$

Assuming that the position of the inert gas atom in the complex corresponds to the lowest potential energy of the system, it is possible to determine the characteristic vibration frequencies of the weak van der Waals bonds:

$$\nu = \frac{1}{2\pi}\sqrt{\left(\frac{\partial^2 e}{\partial r^2}\right)_{r_0}/\mu} = \frac{3 \cdot 2^{1/3}}{\pi\sigma_0}\sqrt{\frac{\varepsilon_0}{\mu}} \ , \qquad (20)$$

where $r_0 = 2^{1/6}\sigma_0$ is the equilibrium interatomic distance.

The steric factors calculated by Eqn. (17) for the reactions 2I + M → product and 2Br + M → product proved to be similar and of the order of 10^{-3} at room temperature, i.e. indeed lower than for bimolecular reactions between atoms. This was in fact to be expected on the basis of of what has been said in Section II, subsection 2. Furthermore, the steric factors were found to increase approximately linearly with temperature, which is contrary to their behaviour in bimolecular reactions. From the standpoint of thermodynamics, such variation indicates that the entropy of activation increases with temperature, i.e. the configurational disorder of the activated complex increases to a greater extent than the disorder of the initial state. Within the framework of the concept of two stages in trimolecular reactions, this implies that the second stage, in which the activated complex is formed from a large number of species and breaks down like a complex species, is rate-determining. The higher is the temperature, the more rapid is the breakdown of the complex. An increase of temperature has the same effect as in monomolecular reactions, although the latter have a positive entropy of activation. The classical pre-exponential factor $A = sz$ increases with temperature together with the steric factor.

We shall now examine the contradictions to which Semenov drew attention [108] using as an example the reaction $Br_2 + M \rightleftharpoons 2Br + M$. It consists in the fact that the equilibrium constant for this process calculated from the ratio of the rate constants for the forward and reverse stages is consistent with the experimental value only under the condition that the steric factor for the dissociation reaction is 10^2, which is unlikely on physical grounds. Indeed, per molecule $k_{rec} \simeq 10^{-32}$ and for binary collisions $z_2 \simeq 10^{-10}$, so that we should have

$$K = \frac{(Br)^2}{(Br_2)} = \frac{s_2 z_2 e^{-Q/RT}}{k_{rec}} \simeq s_2 \cdot 10^{22} e^{-Q/RT} \ , \qquad (21)$$

where Q is the heat (however, in this expression it is assumed that $E_{rec} \simeq 0$, so that $E_{diss} = Q$). At the same time, the equilibrium constant is well known from independent data:

$$K = \frac{(Br)^2}{(Br_2)} \simeq 10^{24} e^{-Q/RT} \ . \qquad (22)$$

The above contradiction can be simply and naturally resolved in the light of the concept of steric factors. The equilibrium constant must be written in the form

$$K = 10^{24} e^{-Q/RT} = \frac{k_{diss}}{k_{rec}} = \frac{s_2 z_2}{s_3 z_3} \frac{e^{-E_2/RT}}{e^{-E_3/RT}} = \frac{s_2 z_2}{s_3 z_3} e^{-Q/RT} \ . \qquad (23)$$

Assuming that z_2 and z_3 are 10^{-10} and 10^{-32} respectively, we obtain for the ratio of the steric factors corresponding to dissociation and recombination $s_2/s_3 \simeq 10^2$, which can be accounted for by the above calculations, showing that $s_3 \simeq 10^{-3}$. The point is that at moderate temperatures the steric and energy factors approximately cancel out¶:

$$\frac{1}{s_3} \simeq e^{-E_3/RT} \ ,$$

and because of this the rate constant is indeed of the same order of magnitude under these conditions as the classical (Tolman) number of collisions [Eqn. (2)]. This fact, already mentioned in section III, subsection 1, can now be fully understood†.

The method described was also used [183], with a somewhat modified model of the activated complex, to interpret the trimolecular homogeneous chain termination reaction $H + O_2 + M \rightarrow HO_2 + M$ in the chain hydrogen combustion process [108,109,118]. The rate constant calculated for this reaction with M = Ar agrees very well with the experimental data of Clyne and Thrush [113] (Table 5). We may

¶For the recombination of halogen atoms in collisions with inert gas atoms, $E_0 = 2-3$ kcal mole^{-1}.

†Keck [195] showed by a statistical procedure that the rate constant for the recombination process at low temperatures must be close to the classical number of three-body collisions.

note that this calculation allows some improvement in the solution of the problem of the temperature variation of the upper explosion limit, which is regulated by the competition between this reaction and the chain-branching reaction $H + O_2 \rightarrow OH + O$.

Umanskii and Stepukhovich [196] calculated the kinetic characteristics of certain other reactions of the type $A + BC + M \rightarrow ABC + M$. An analogous approach may be employed to interpret the effect of the third body in the recombination of radicals at low pressures, where the rate is determined by the "pure" third-order constant. Umanskii and Stepukhovich [196,197] suggested that in the second stages of radical recombination by ET and RMC mechanisms the same activation complex is formed. Then the three-body recombination rate constants (at low pressures) are

$$k^{ET} = A^{\neq}\left(\frac{E^*}{RT}\right)^{m-1}\frac{1}{(m-1)!}\ , \qquad (24)$$

$$k^{RMC} = A^{\neq}\exp\left(\frac{\Delta E}{RT}\right)\ , \qquad (25)$$

the expressions involving the same pre-exponential factor $A^{\neq}$ defined by the TST formulae. E^* is the energy distributed among m internal degrees of freedom in the first stage of the ET mechanism and ΔE the energy of formation of the radical-molecular complex.

It is qualitatively clear that the energy transfer mechanism is more likely in the recombination of complex radicals, since it postulates the formation of an intermediate compound with a larger number of internal degrees of freedom and consequently with a longer lifetime (at least in the case of simple third bodies).

Here the concept of the "loose" activated complex was employed [194,198,199]. It is now generally accepted that in bimolecular radical recombination reactions a complex of this kind is in fact involved. Nevertheless in the early studies [15] it was shown that, whereas the number of two-body collisions of relatively simple particles may be fairly well estimated on the basis of rigid molecular models, it is evident that no three-body collisions can involve absolutely rigid molecules. This applies to an even greater extent to complex polyatomic species‡.

On the basis of these considerations, the third-rate order rate constant for the symmetrical recombination of certain alkyl radicals with straight-chain [200] and branched-chain [200] structures and the rate constants for unsymmetrical recombination [197] were calculated. In the latter case it was found that, if in the reaction $R' + R'' + M \rightarrow$ product, the recombining radicals differ markedly in the degree of their complexity, the rate constant may greatly exceed the geometrical mean of the constants for the symmetrical recombination reactions $R' + R' + M \rightarrow$ product and $R'' + R'' + M \rightarrow$ product. The pre-exponential factors for all these reactions proved to be very similar. The steric factor was found to be lower than for atomic recombination due to increase in steric hindrance. Generalising the results of the above discussion of steric factors for three-body recombination reactions involving various species, one may conclude that the following characteristic features obtain:

Recombination of atoms: $s \simeq 10^{-3};\ \frac{ds}{dT} > 0$,

Recombination of atoms with simple molecules: $s \simeq 10^{-3} - 10^{-4};\ \frac{ds}{dT} \simeq 0$,

Recombination of complex radicals: $s \leqslant 10^{-5};\ \frac{ds}{dT} < 0$.

‡The considerations adduced above concerning the relation between the steric factors for trimolecular and bimolecular reactions do not of course refer to the free activated complex model.

The knowledge of the calculated third-order rate constants permit the prediction of the pressure ranges where the order of the reaction changes provided that the experimental second-order rate constants describing the recombination at high pressures [197] are known. The characteristic transition pressure is higher the higher the temperature and the simpler the recombining radicals and the third body.

Examination of the elementary step characteristic of TST, with the aid of the potential energy surface was subsequently applied also in combination with various simplified interaction models whereby the dynamics of three-body collisions may be described mathematically. We may note, for example, the idealised theory of atomic recombination proposed by Jepsen and Hirschfelder [201]. In this theory the calculation of the rate of recombination of atoms in a colinear three-body collision requires the determination of the individual collision trajectories in order to find the fraction of activated complexes decomposing into recombination products. These authors examined an idealised interaction potential for three atoms located on a single straight line in the form

$$V = v(r_{12}) + v(r_{23})\ , \qquad (26)$$

the potential $v(r)$ being approximated by the rectangular potential well model. The potential energy surface corresponding to this model is shown in Fig. 5*a* in skewed coordinates (the angle between the axes is 60°, since the masses of all three atoms are assumed to be identical).

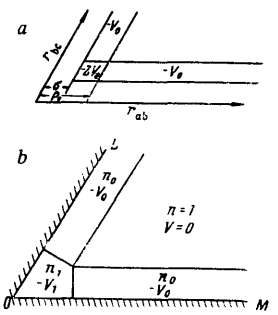

Figure 5. Potential energy surface in the idealised theory [201].

The surface consists of a plateau in the upper right-hand corner (dissociated state), two "trenches" with sheer walls parallel to the coordinate axes (two possible associated states), and a "well" in the lower left-hand corner of the diagram (activated complex or a metastable triatomic molecule). However, in order to facilitate the calculations, a somewhat different surface was employed (Fig. 5*b*) and for the sake of generality the depth of the well V_1 was assumed to be arbitrary. The motion of the representative point with a specified energy E over such a surface exhibits complete analogy with geometrical optics if a refractive index $n = [(E - V)/E]^{1/2}$ is assigned to each part of the surface. This motion is characterised by a linear trajectory which undergoes reflection and refraction at the discontinuities in the potential. It is limited by the internal region of the angle *LOM* in Fig. 6*a* ("the region of motion"), and the trajectories can be studied particularly

conveniently when this region is expanded on the kaleidoscope principle (Fig. 6*b*). The task thus reduces to the determination of the flux of representative points per unit time across the DB_0E line which ensures recombination, i.e. the corresponding trajectories no longer re-emerge from the region of bound states.

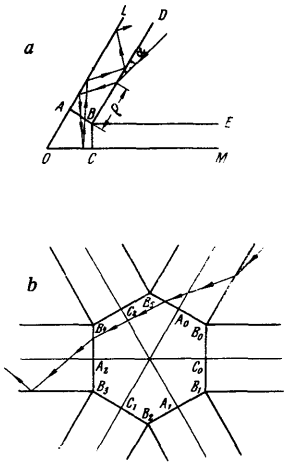

Figure 6. Idealised theory[201]. Trajectory of the representative point: *a*) in the "region of motion"; *b*) in the expanded form.

The aim of any treatment of this kind reduces to finding a formula for the frequency of the effective three-body collisions where only the masses and diameters of the reacting species are included as parameters (we may recall that simple kinetic formulae for the number of three-body collisions contain an undefined parameter characterising the region of operation of intermolecular forces). In his discussion of the contribution of essentially simultaneous three-body collisions to the overall rate of recombination, Smith[202] holds the same view. For a symmetrical description of the motion of three particles in a six-dimensional space, we must construct three three-dimensional cylinders representing the pair interactions between atoms (a "cut off" potential of pair interaction is considered). These cylinders intersect in the region S near the origin of coordinates where all three species interact simultaneously. In those parts where there is no interaction the trajectory is linear and it can enter the region S either directly ("pure" three-body collision) or indirectly, passing first through one of the cylinders and forming a diatomic complex before collision with a third particle. The determination of an effective collision cross-section requires the determination of a geometrical section through the region S. Smith[202] gives an approximate estimate of this section for the case where two of the three reacting atoms are identical. Comparison of the results of the calculations with the experimental data of Christie et al.[121] for the reaction 2I + M → product (Table 4) showed that at 293°K the effectiveness of the simultaneous three-body collisions in the recombination is of the order of 10^{-2}–10^{-3} (1/44 for M = Xe and 1/720 for M = He), the effectiveness being greater the closer is the mass of the third body to that of the recombining atom.

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Department of Chemical Physics,
Saratov State University

U. D. C. 543.253 : 547.52/53

Polarography of Benzenoid Aromatic Hydrocarbons

S.I.Zhdanov

This review summarises the results of the study of the reduction and oxidation in protogenic, aprotic, and strongly acidic solutions of benzenoid polynuclear aromatic hydrocarbons whose molecules do not contain electrochemically active substituents. The characteristic features of the adsorption of aromatic hydrocarbons on mercury and various other metals are noted. The bibliography contains 167 references.

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I. INTRODUCTION

The investigation of the problem of aromaticity[1,2], resulting to a considerable extent from the outstanding progress in the field of quantum chemistry, has led to the publication of a large number of papers on the study of the polarographic properties of aromatic compounds. This is due primarily to the fact that the polarographic method is an extremely convenient method for studying the mechanism of electrode processes and can be successfully used to verify theoretical conclusions by correlating polarographic half-wave reduction and oxidation potentials ($E_{1/2}$) with the energy parameters of the molecules, obtained by quantum-chemical calculations. It is now an appropriate time to systematise this extensive published material, which includes valuable information of interest to a wide circle of chemists. These papers have of course been examined in reviews devoted to the polarography of organic compounds, but the treatment has been incomplete[3-8]. The most successful review of these papers is that of Peover[9], but this is published in a source not readily available to Soviet readers, and a number of problems were not examined in it.

The present review to some extent fills this gap. It includes papers on the polarography of only those benzenoid aromatic hydrocarbons which do not contain electrochemically active substituents, and also on the polarography of unsaturated compounds, but only to the extent necessary for an understanding of the phenomena examined. A review of papers on the polarography of non-benzenoid aromatic hydrocarbons was published separately[10].

II. MECHANISM OF REDUCTION

The reduction of unsaturated and aromatic hydrocarbons at a dropping mercury electrode is generally studied in a supporting electrolyte of tetra-alkylammonium salts, most frequently $(C_4H_9)_4NI$, since in solutions of these salts the processes taking place at the most negative potentials can be studied. The second electrode is usually a layer of mercury in contact with the solution being studied; the potential of the second electrode is measured relative to an aqueous saturated calomel electrode. When the values of $E_{1/2}$ are compared, it is not necessary to allow for the inter-phase potential at the interface between the aqueous KCl solution and the non-aqueous $(C_4H_9)_4NI$ solution.

To establish the mechanism of the electrode processes and in particular to obtain the polarographic characteristics ($E_{1/2}$), which can be correlated with the energy parameters of the molecules, it is very important to carry out the studies in solvents with low proton activity ("availability"). It was in so-called aprotic solvents that the stages of reversible electron transfer with the formation of fairly stable hydrocarbon anion radicals, almost uncomplicated by subsequent irreversible reactions of protonation, dimerisation, or disproportionation, were revealed. This behaviour is in complete accordance with the general empirical rules formulated by Stackelberg[11,12] (see also Ref. 3) on the basis of extensive experimental material.

1. The stage of electron transfer is reversible if the geometric structures of the starting material and product do not differ significantly.

2. The stage is irreversible if it is accompanied by the formation of stable σ bonds, for example C–H (protonation) or C–C (dimerisation) bonds.

3. The stage is irreversible if it is accompanied by rupture of a stable σ bond, for example the bonds C–Hal in halogen derivatives, O–O in peroxides, and N–O in hydroxylamines.

4. The stage is irreversible if it is accompanied by the attachment of a proton to a heteroatom with the formation of N–H or O–H bonds, since these bonds are kinetically labile.

The study of aprotic solvents in the polarography of organic compounds was begun by Wawzonek and coworkers[13-18]. Wawzonek was the first to use a dioxan–water (3 : 1) mixed solvent[13-15], and subsequently acetonitrile, dimethylformamide[16,17], and tetramethylurea[18].

Many other authors used solvents which are not strictly aprotic: 75% dioxan[18-34], 85% dioxan[35,36], 96% dioxan[23,25-27,37], 75% ethanol[36,38], ethylene glycol monomethyl ether (cellosolve)[39-41], 50% isopropyl alcohol[42], a tetrahydrofuran–water mixture (3 : 1)[43], and ethylenediamine[44]. Other authors, like Wawzonek, used purely aprotic solvents: dimethylformamide (DMFA)[45-60], acetonitrile[61,62], and

tetrahydrofuran[63]. Purely dioxan solutions have not yet been used in polarography, because of the very low electrical conductivity. DMFA is most frequently used. Similar polarographic properties are shown by tetramethylurea, but this solvent has not found extensive application.

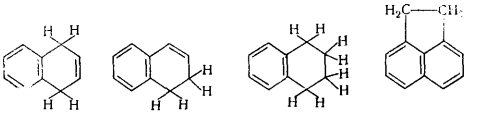
Simple unsaturated and aromatic compounds are reduced at a dropping mercury cathode in the range of high cathode potentials. Compounds whose molecules contain a single non-activated multiple bond[13] or benzene ring[14] are not reduced at all at a dropping mercury cathode in a range of potentials which can be measured. Aliphatic unsaturated compounds with conjugated bonds undergo two-electron reduction in 75% dioxan[20]. For allene ($CH_2=C=CH_2$), $E_{1/2}$ = -2.33 V, for butadiene ($CH_2=CH-CH=CH_2$), $E_{1/2}$ = -2.63 V, etc.

Vinylacetylene ($CH\equiv C-CH=CH_2$) gives two two-electron waves with $E_{1/2}$ = -2.44 V and -2.62 V. The first wave corresponds to the reduction of the triple bond to a double bond, and the second wave corresponds to the reduction of the butadiene produced. Thus the reduction of unsaturated compounds involves the hydrogenation of multiple bonds. Reduction is complete when the compound contains one or several non-conjugated and non-activated multiple bonds.

The reduction of compounds with multiple bonds activated by conjugation with phenyl rings takes place in exactly the same way[13,20]. In these compounds, the multiple bonds undergo electrochemical hydrogenation, whereas the phenyl rings are not attacked. Reduction is complete when the compound does not contain multiple bonds conjugated with other multiple bonds or with phenyl rings.

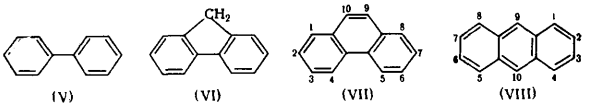
Increase in the conjugation facilitates reduction: $E_{1/2}$ becomes less negative in the series styrene ($Ph-CH=CH_2$), 1,1-diphenylethylene ($Ph_2=C=CH_2$), stilbene (Ph-CH=CH-Ph), triphenylethylene ($Ph_2=C=CH-Ph$), and tetraphenylethylene ($Ph_2=C=C=Ph_2$). The double bond is activated to a greater extent and is therefore more readily reduced when the two phenyl groups are arranged symmetrically with respect to the double bond (stilbene), than when they are arranged unsymmetrically (1,1-diphenylethylene). Styrene is more readily reduced than β-methylstyrene ($Ph-CH=CH-CH_3$), the effect of the methyl group being considerable ($\Delta E_{1/2} \simeq 200$ mV). 1,4-Diphenylbutadiene (Ph-CH=CH-CH=CH-Ph) gives only one wave corresponding to two-electron reduction. Thus this compound is attacked in the 1,4-position, and the molecule of the product contains one of the double bonds in the middle of the carbon chain, not conjugated with either of the two phenyl rings. Phenylacetylene ($Ph-C\equiv CH$) and diphenylacetylene ($Ph-C\equiv C-Ph$) have more negative $E_{1/2}$ values than styrene and stilbene, and they therefore undergo immediate four-electron reduction with the formation of ethylbenzene and bibenzyl respectively.

An analogous picture is observed in the reduction of aromatic hydrocarbons[14]. In the naphthalene molecule, only one double (more accurately aromatic) bond is hydrogenated. From this it follows that the reduction product is 1,5-dihydronaphthalene (I), in whose molecule the double bond is not conjugated with the phenyl ring. 1,2-Dihydronaphthalene (II) is reduced to tetralin (III), which does not exhibit electrochemical activity:



(I) (II) (III) (IV)

Acenaphthene (IV) is reduced in the same way as naphthalene: it gives only one two-electron wave. Biphenyl (V) and fluorene (VI) are hydrogenated in the 1,4-position.



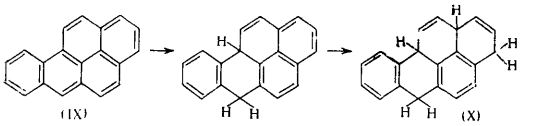
(V) (VI) (VII) (VIII)

The molecules of the products of the two-electron reduction contain only isolated double bonds and a phenyl ring.

Phenanthrene (VII) gives two two-electron waves, the value of $E_{1/2}$ for the second wave being close to the value of $E_{1/2}$ for 9,10-dihydrophenanthrene, and also biphenyl and fluorene. On this basis, the first wave for phenanthrene is attributed to the reduction of the double bond in the 9,10-position, and the second wave to reduction similar to the reduction of biphenyl and fluorene.

Anthracene (VIII) gives one two-electron wave, from which it follows that it is characterised by hydrogenation in positions 9 and 10 with isolation of the two phenyl rings.

Other polynuclear aromatic hydrocarbons studied by Wawzonek (chrysene, pyrene, 1,2-benzanthracene, 1,2,5,6-dibenzanthracene, and 3,4-benzpyrene) give multi-wave polarograms with characteristic rapid breakdown of the molecule into isolated double bonds and phenyl rings. Thus of the ten aromatic bonds in 3,4-benzpyrene (IX)



(IX) (X)

only two are reduced, with the formation of compound (X), where the molecule contains two isolated phenyl rings and two isolated bonds.

The values of $E_{1/2}$ for the waves corresponding to the reduction of unsaturated and aromatic compounds are independent of pH (at pH > 7). The slope of the straight line obtained by plotting $\lg i/(i_d - i)$ against E is 0.06-0.07 V, that is it, as it were, corresponds to the theoretical slope (0.059 V) for a reversible potential-determining one-electron reaction. On this basis, Wawzonek[13] proposed the following mechanism of reduction:

$$R + e = R^{\cdot-} \text{ (reversible potential-determining state)} \quad (1)$$
$$R^{\cdot-} + e \rightarrow R^{2-} \text{ (irreversible stage)} \quad (2)$$
$$R^{2-} + 2H_2O \rightarrow RH_2 + 2OH^- \text{ (irreversible rapid stage)} \quad (3)$$

A second possible mechanism:

$$R + e = R^{\cdot-} \quad (1)$$
$$R^{\cdot-} + H_2O \rightarrow RH^{\cdot} + OH^- \quad (4)$$
$$RH^{\cdot} + e = RH^- \quad (5)$$
$$RH^- + H_2O \rightarrow RH_2 + OH^- \quad (6)$$

was also examined[13], but it was rejected, since for this mechanism $E_{1/2}$ should have been dependent on pH, and this is not observed experimentally. Subsequent studies showed, however, that most compounds are nevertheless reduced according to the second mechanism.

Considerable progress in the study of the mechanism of the reduction of aromatic and unsaturated compounds has been made by applying quantum-chemical calculations to polarographic data. The foundations for this work were laid in a short note published by Maccoll[64]. By developing Hückel's idea of the existence of a relationship between the

energy of the lowest vacant π electron molecular orbital, into which the molecule can accept one or two electrons, and the ease of attachment of alkali metals to aromatic compounds, Maccoll observed a relationship between the reduction potential of an aromatic compound and the energy of the lowest vacant molecular orbital (MO).

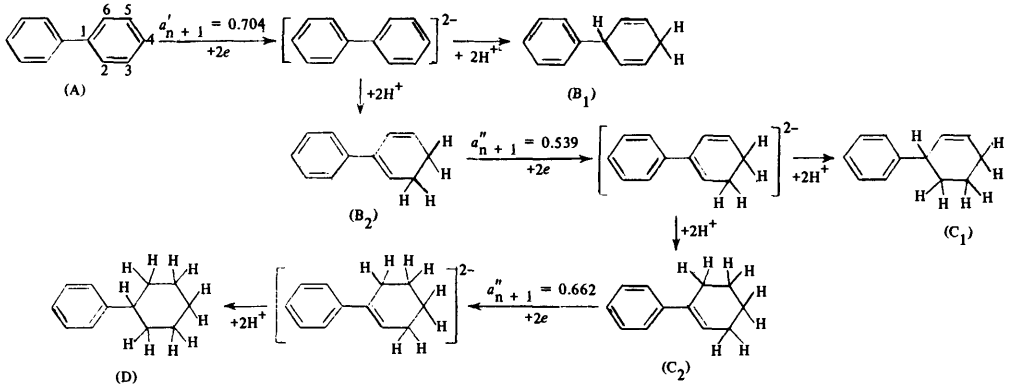
The best known subsequent papers are those of Hoijtink. In his first paper[22] he derived the relationship between $E_{1/2}$ and energy of the lowest MO:

$$E_{1/2} = a_{n+1}\beta - 1.05 \qquad (7)$$

(where a_{n+1} is a coefficient characterising the energy of the lowest vacant MO, β the exchange or resonance integral, and 1.05 the value of $E_{1/2}$ for the first wave of triphenylmethyl, taken as standard), and also put forward arguments which make it possible on the basis of these data to predict the direction of the process. Since $\beta < 0$ ($\beta \simeq -2.27 \pm 0.07$ eV [22]), the value of $E_{1/2}$ is more negative, the larger a_{n+1}.

Eqn. (7) is useful chiefly because it can be used to calculate $E_{1/2}$ for the starting material and the assumed products of the two-electron reduction. If the product has a more negative $E_{1/2}$ value than the starting material, the polarogram will show two two-electron waves; if it has a less negative $E_{1/2}$ value, one four-electron wave will be produced. Thus if the value of a_{n+1} for the starting material is greater than the value of a_{n+1} for the product, four-electron reduction ($n = 4$) should take place immediately.

The calculation also makes it possible to make predictions regarding the structure of the product. If we accept the mechanism of reduction proposed by Wawzonek[13] (reactions 1–3), the structure of the product (intermediate or final) will be determined by the distribution of the π electrons over all the carbon atoms of the framework of the molecular doubly-charged anion R^{2-} and the radical-anion $RH^{\cdot}$, since their protonation (reaction 3) will have the greatest probability at the carbon atom at which the negative charge is a maximum[64]. Hoijtink states[22] that consideration of the other mechanism (reactions 1, 4–6) leads to the same results. For example, for the reduction of biphenyl:



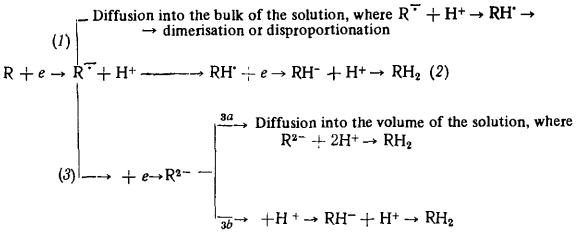
Calculations show that $a'_{n+1} > a''_{n+1}$ and $a'_{n+1} > a'''_{n+1}$. Thus all three substances, that is A, B_2, and C_2, should give a single reduction wave. Moreover, according to the calculation, in the AH^- anion obtained by the attachment of the first proton to the doubly-charged anion A^{2-}, the π electron density should be the same at the carbon atoms in positions 1, 3, and 5. Since positions 3 and 5 are identical, one third of the biphenyl (A) should be reduced to B_1, and two thirds to B_2. Of these two products, only B_2 can undergo further reduction, since B_1 contains only isolated double bonds. Thus the number of electrons in the second stage of the reduction, calculated on the biphenyl, is $n_2 = n_1 2/3 = 4/3$. For the same reasons, half of the intermediate product B_2 is reduced to the product C_1, which does not show polarographic activity, and half is reduced to C_2, which undergoes reduction to the polarographically inactive product D. The number of electrons in the third stage is $n_3 = n_2 1/3 = 2/3$, and the overall wave should correspond to the transfer of $n_{total} = n_1 + n_2 + n_3 = 2 + 4/3 + 2/3 = 4$ electrons. A mixture of products consisting of equal quantities of B_1, C_1, and D should be formed.

This examination was carried out for 12 aromatic hydrocarbons, and very good agreement was obtained between the values of $E_{1/2}$ and the experimental values[14] if allowance is made for the approximate nature of the method of calculating the values of a_{n+1} and the derivation of Eqn. (7).

An analogous approach was used in the examination of the reduction of diphenylpolyenes[37] with general formula $Ph-(CH=CH)_m-Ph$ ($m = 2-6$). For all the compounds studied, $a'_{n+1} < a''_{n+1} < a'''_{n+1}$ etc. Thus the diphenylpolyenes give separate waves for the reduction of individual double bonds.

Application of Wawzonek's mechanism led Chopard-dit-Jean and Heilbronner[65] to the conclusion that there is a difference in the mechanisms of reduction of alternant (for example naphthalene) and non-alternant (for example azulene) aromatic hydrocarbons. In their opinion, alternant hydrocarbons always give two-electron waves, whereas non-alternant hydrocarbons may give one-electron and two-electron waves. Hoijtink and coworkers[25] criticised this view and showed that in an aprotic medium both alternant and non-alternant hydrocarbons give a first one-electron wave. When even weak proton donors (e.g. water) are added, this wave in most instances becomes a two-electron wave. The first wave for azulene, however, even under these conditions, remains a one-electron wave, the reason for which will be examined below.

On the basis of these experimental results, the following general mechanism was proposed



In contrast to the mechanism of Laitinen and Wawzonek, it is assumed that $E_{1/2}$ for the attachment of the first electron is less negative than $E_{1/2}$ for the attachment of the second electron (path 3). On the other hand, $E_{1/2}$ for $RH^{\cdot}$ is always less negative than $E_{1/2}$, since a_{n+1} for this species is smaller than that for the original molecule R. Thus in the absence of proton donors, or when the protonation of the radical-anion $R^{\cdot-}$ is too slow (path 1), the attachment of only one electron takes place at the potentials of the first wave; the radical-anions formed diffuse into the bulk of the solution, where they are slowly protonated and either dimerise or disproportionate. At more negative potentials, the second electron is attached (path 3), and the doubly-charged anion is protonated. The second wave often corresponds to the transfer of more than one electron. This means that R^{2-} has a higher affinity for the proton and is able to undergo protonation in direct proximity to the electrode. If the new molecule RH_2 can undergo further reduction, this process also increases the second wave. The electron affinity of $R^{\cdot-}$ is less than that of RH_2 for, for example, perylene, coronene, fluoranthene, azulenes, and decacyclene.

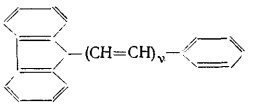
If the rate of protonation of the anion-radical $R^{\cdot-}$ is greater than the rate of diffusion of $R^{\cdot-}$, the $RH^{\cdot}$ radicals formed close to the electrode add on a second electron, the first wave is increased, and the wave for the reduction of $R^{\cdot-}$ at more negative potentials disappears. Path 3 can of course still be realised at these potentials, since in the final analysis increase in the cathode potential makes path 3 more rapid than path 2.

In experiments with the addition of weak proton donors, an intermediate case, where the rates of the diffusion and protonation of $R^{\cdot-}$ are commensurate, has been realised. As a result of simultaneous reduction by paths 1 and 2, the first wave acquires an intermediate height ($2 > n > 1$).

To obtain more information on the mechanism a detailed study has been made of the influence of the concentration of proton donors and the concentration of depolariser on the form of the waves and the magnitude of $E_{1/2}$.[25] An approximate method involving the use of the Nernst equation and the material balance equations was used to derive equations for the wave and $E_{1/2}$, which were compared with experiment. It is obvious that this derivation is inapplicable, if the transfer of both the first and the second electrons takes place reversibly. It has been shown[26] that the Nernst equation can be used if the rates of electron transfer in both directions are appreciably greater than the rates of the diffusion and attachment of protons to the anions.

Analysis of the properties of the waves for hydrocarbons in the presence of weak proton donors, again by an approximate method, made it possible to obtain relationships which correspond, qualitatively at least, to the experimental results. In this way, the new mechanism has to a large extent been confirmed.

In subsequent work, Hoijtink[26] extended the measurements to 1-phenyl-*p*-biphenylenepolyenes, 1-phenyl-*p*-(2,3-benzo)-biphenylenepolyenes, and dibiphenylenepolyenes in 75% and 96% dioxan. In 96% dioxan, the compounds studied gave polarograms with either two one-electron waves or one two-electron wave. It was shown that in the first instance the reduction takes place by Hoijtink's mechanism[25]. In the second instance, two mechanisms are possible: Hoijtink's mechanism (high proton affinity of $R^{\cdot-}$, leading to rapid protonation of $R^{\cdot-}$ and slow reduction of $RH^{\cdot}$) and the mechanism of Laitinen and Wawzonek (electron affinity of $R^{\cdot-}$ greater than that of R). Hoijtink was able to show that here the reduction (two-electron) takes place by the mechanism of Laitinen and Wawzonek. He observed the following relationship: the values of $E_{1/2}$ for both waves of 1-phenyl-*p*-biphenylenepolyenes (XI):



(XI)

become less negative with increase in the length of the polyene chain (with increase in ν), but in such a way that the difference in $E_{1/2}$ decreases. At $\nu = 6$, the values of $E_{1/2}$ for the two waves coincide. Analysis of the properties of the waves by means of a method similar to that just described showed that for substances which give two-electron waves in 96% dioxan, the reduction takes place by the mechanism of Laitinen and Wawzonek.

These results show that in the electrochemical reduction of hydrocarbons, direct transfer of electrons to the molecule being reduced takes place with the formation of radical and molecular carbanions. These anions are unstable towards protonation, but it might be expected that they would have appreciable stability in aprotic media. Various compounds, even in 96% dioxan, that is in a medium which is not strictly aprotic, give two one-electron waves on the polarograms. The radical-anions are evidently fairly stable even under these conditions. The direct observation of the formation of radical-anions and the study of their properties was of considerable interest. This problem was solved in two ways: by electrolysis in acetonitrile or DMFA[16] and by reaction with alkali metals in dimethoxyethane or tetrahydrofuran[66,67].

In acetonitrile and DMFA, a number of the compounds studied form one-wave polarograms ($n = 2$ for styrene, triphenylethylene, and tetraphenylethylene), whereas stilbene, anthracene, and 9-anisylidenefluorene give two waves of unequal height[16]: the first wave is appreciably higher than the second and on the addition of water or benzoic acid (in lower concentration) the first wave increases until it becomes the only wave.

Electrolysis of solutions in acetonitrile or DMFA on a large stationary mercury cathode in all instances produces an intense colour in the solution, characteristic of solutions of radical-anions. The products of the electrolysis of stilbene in DMFA were found to contain 1,2,3,4-tetraphenylbutane, which is evidently obtained by dimerisation of the radical-anions. Further proof of the existence of stable radical-anions was provided by the isolation of dicarboxylic acids from the products of the electrolysis of stilbene in the presence of carbon dioxide.

The reaction of metallic sodium with an aromatic hydrocarbon in dimethoxyethane or tetrahydrofuran gives a salt-like compound of sodium and the hydrocarbon, in which the hydrocarbon forms the anionic part. These compounds

are readily soluble in dimethoxyethane and in tetrahydrofuran and are completely or partly (for the disodium compound) dissociated.

Use has been made[66,67] of the fact that a solution of sodium biphenyl can be used to titrate solutions of other hydrocarbons which have a higher electron affinity than biphenyl. If the potential of the indicator electrode is measured, it is possible to determine the normal potentials of the hydrocarbons (relative to the potential of biphenyl). If the potential for the transfer of a second electron is sufficiently high, the titration may also give the radical-anion and the doubly-charged anion. Experiment showed that the values of the normal potentials obtained in this way are close to the values of the polarographic $E_{1/2}$, the difference in the values of $E_{1/2}$ for the first and second stages amounting to 0.4–0.6 V. The absorption spectra of the radical-anions of aromatic hydrocarbons have been measured[68] and it has been shown[69,70] that these spectra can be interpreted by the methods of quantum chemistry.

The spectra of the radical-anions on the one hand and of the doubly-charged anions on the other[71] have characteristic absorption bands, all the bands being displaced towards longer wavelengths with increase in the length of the conjugated system of double bonds (from stilbene to diphenyldodecahexaene). The reactions of radical-anions with aromatic hydrocarbons exhibiting a less negative half-wave potential have also been studied by EPR spectroscopy[60].

In their discussions, Hoijtink and coworkers suggested that the transfer of electrons to the hydrocarbon molecule and the hydrocarbon radical-anion takes place reversibly; the reversibility was proved by the methods of classical polarography (form of the wave). More rigorous proof can be obtained by alternating-current polarography, in which the reversible processes are characterised by the Faraday current peaks, which exhibit definite properties[72–74]. Hoijtink and coworkers studied the reduction of aromatic hydrocarbons and diphenylpolyenes in DMFA by alternating-current polarography and obtained the following results[47,48,51,57,75].

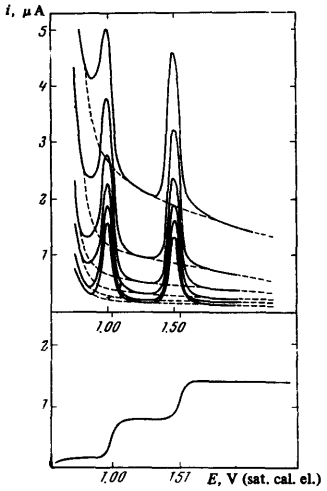


Figure 1. Alternating-current and classical polarograms for dibiphenyleneethylene in dimethylformamide. Frequency, Hz (from lower curve to upper): 32.1, 43.1, 62.5, 94.0, 174, and 392 (published data[47]).

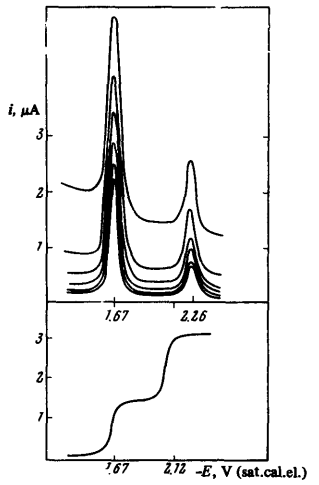


Figure 2. Analogous data for perylene in dimethylformamide.

The properties of the radical-anions of α,ω-diphenylpolyenes and tetraphenylcumulenes, that is compounds of the type $Ph_2=C=C=C=C=Ph_2$ (tetraphenylbutatriene) were studied in exactly the same way[71]. It was observed that the difference in the normal potentials of the first and second one-electron stages (and hence $\Delta E_{1/2}$) for these compounds is much smaller (~ 0.20 V) than that for aromatic hydrocarbons (0.4–0.6 V). The cumulenes are reduced much more readily than the polyenes, since the conjugation in the former is stronger. Polarographic study of tetraphenylbutatriene in DMFA and in aqueous dioxan solutions[53–55] confirmed these results. The intermediate products are tetraphenylbutadiene and tetraphenylbut-1-ene, in which the double bonds are conjugated with the phenyl groups and are reduced further. The final products are tetraphenylbut-2-ene (with an isolated double bond) and tetraphenylbutane.

The alternating-current polarograms for solutions of dibiphenyleneethylene (Fig. 1) and dibiphenylenebutadiene show two Faraday current peaks, corresponding to the two waves on the classical polarograms; on the alternating-current polarograms for aromatic hydrocarbons (tetracene, perylene, fluoranthene, anthracene, coronene, pyrene, 1,2-benzpyrene, and naphthalene) the second peak is always lower than the first peak (Fig. 2)[47]. Judging from the frequency dependence of i_f for both peaks of dibiphenyleneethylene and dibiphenylenebutadiene, both electrons are transferred reversibly. The second electron in the reduction of aromatic hydrocarbons is transferred irreversibly. It is suggested that the irreversibility of the transfer of the second electron for aromatic hydrocarbons is due to R^{2-} protonation, which, thanks to the high proton affinity of R^{2-}, takes place rapidly even in DMFA.

The first stage in the reduction of α,ω-diphenylpolyenes in DMFA is also reversible[48]. On the classical polarograms, however, the first wave is appreciably higher than the second (with the exception of stilbene, whose polarogram consists of two waves of equal height), and on going to higher α,ω-diphenylpolyenes, a tendency for the first wave to increase further at the expense of the second is observed. The second peaks on the alternating-current polarograms of all α,ω-diphenylpolyenes decrease with increase in the frequency of the applied alternating potential, indicating that the second stage of the reduction is irreversible (due to the protonation of R^{2-}). The increase in the first wave at the expense of the second is related to the protonation of the radical-anions $R^{\cdot-}$; the proton affinity of $R^{\cdot-}$ increases with increase in the number of double bonds in the α,ω-diphenylpolyenes. These experiments, however, do not give an unambiguous indication of the reason for the irreversibility of the second stage of the reduction, since it may also be due to slow transfer of the second electron to the radical-anion $R^{\cdot-}$. It has been pointed out[51] that the kinetics of this stage may be influenced by the structure of the electrical double layer.

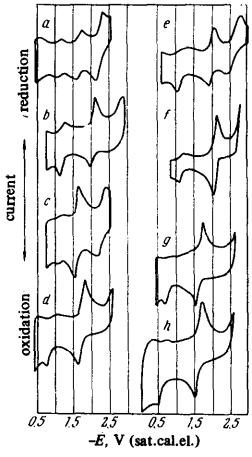


Figure 3. Cyclic polarograms in 0.1 M $(C_4H_9)_4NClO_4$ in dimethylformamide on a stationary platinum electrode for the two-electron reduction of: *a*) perylene; *b*) pyrene; *c*) tetracene; *d*) fluoranthene; *e*) 1,2-benzanthracene; *f*) coronene; *g*) acenaphthylene; *h*) acridine. 50 pulses per second (published data[76]).

It was later confirmed by cyclic volt-ammetry with a platinum electrode[76] or hanging mercury drop electrode[77] that the first stage in the reduction of polynuclear aromatic hydrocarbons (perylene, pyrene, tetracene, and various others) in an aprotic medium is reversible, whereas the second stage is partly or completely irreversible; the anodic branch of the cyclic volt-amperogram shows a clearly defined peak due to oxidation of the radical-anion, whereas the peak for the oxidation of the doubly-charged anion is either very small or completely absent (Fig. 3).

The question of whether it is possible in principle to achieve the electrochemical preparation of triply-charged radical-anions of aromatic hydrocarbons by the attachment of three electrons is of considerable interest. It has been reported[78] that the electrolysis of tetracene in acetonitrile at −2.5 V gives radical species whose EPR signal differs from that of the singly-charged tetracene radical-anion. Hoijtink[57] showed by alternating-current polarography that these experiments actually gave the singly-charged dihydrotetracene radical-anion. The alternating-current polarogram of tetracene shows two Faraday current peaks, corresponding to the first and third waves on the classical polarogram of tetracene. This means that the second stage of the reduction of tetracene is irreversible, because of the rapid protonation of R^{2-} with the formation of dihydrotetracene, whose molecule still contains the naphthalene aromatic system. The third wave on the classical polarogram and the second peak on the alternating-current polarogram thus correspond to the transfer of a single electron to the dihydrotetracene molecule with the formation of the radical-anion. This of course does not mean that the formation of triply-charged radical-anions is in general excluded, but the probability of their production is low, because of their extremely high proton affinity.

We see that the application of the methods of quantum chemistry makes it possible to predict the path for the reduction of complex aromatic and unsaturated compounds. In practice, however, the most probable route is not always realised. For example, according to theory, biphenyl should undergo four-electron reduction in one wave with the formation of a mixture of three substances[22], whereas the experimental results[14] show that it gives only one two-electron wave.

To explain these discrepancies, Hoijtink introduced the idea that the electrical field of the double layer on the electrode or of the counter-ions in solution (primarily protons) influences the electron density distribution in the doubly-charged hydrocarbon anions, determining the nature of the product in the first stage of the reduction[79,80]. In the Soviet literature, this view is held in particular by Bezuglyi[81-83]. Calculations showed[79] that up to a field strength of 1.5 V/Å the negative charge in the doubly-charged naphthalene anion remains greatest in the peri-positions (1,4 or 5,8), whereas in the doubly-charged anions of anthracene, phenanthrene, pyrene, and terphenyl, under the influence of the electric field, the negative charge may be greatest at positions which are not the positions at which it is a maximum in the absence of the field. The change in the reaction centre in the doubly-charged anion takes place at a field strength of about 0.6 V/Å for anthracene, at a strength of about 0.2 V/Å for phenanthrene, and at the even smaller strength of 0.12 V/Å for terphenyl. Thus if the aromatic hydrocarbon is reduced in a protonic solvent and its doubly-charged anion is protonated on the electrode surface, the electric field at the electrode can in principle influence the direction of the process. For example, for anthracene it has been shown theoretically that the primary product is 9,10-dihydroanthracene at field intensities below 7×10^7 V/cm, and 1,4-dihydroanthracene at higher field intensities. In the first instance the molecule has two isolated benzene rings, and under the conditions of polarography, 9,10-dihydroanthracene will be the final product. In the second instance, the molecule of the product still contains a naphthalene system and an isolated double bond. A second wave due to reduction of the naphthalene group should therefore be observed. Hoijtink pointed out the generality of the mechanism of the electrochemical, chemical, and catalytic hydrogenation of aromatic and arylethylenic hydrocarbons (with the primary attachment of one or two electrons to the molecule being reduced). On this basis, he introduced into the analysis of the experimental results data on not only the electrochemical reduction (primarily polarographic data), but also

on chemical reduction (by alkali and alkaline earth metals in inert and proton-active solvents) and on catalytic hydrogenation. These results for the most part agree with the conclusions of the theory. By comparing the compositions of the products obtained under different conditions with the theoretical schemes, it is possible to estimate the magnitude of the electric field gradient under the conditions of a given experiment. For example, the catalytic hydrogenation of anthracene in a solvent of low dielectric constant gives a mixture of 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene, whereas more severe hydrogenation conditions give a mixture of symmetrical and unsymmetrical octahydroanthracenes. This means that the intensity of the field acting on the doubly-charged anion under these conditions is $(6-7) \times 10^7$ V/cm.

From this interesting and important work it follows that the reduction of even fairly simple aromatic hydrocarbons is a complex process. Thus if an organic compound gives a polarogram with two two-electron waves, determination of the nature of the product in the first stage of the reduction is not sufficient to enable a definite conclusion to be reached regarding the nature of the product in the second stage of the reduction. In general, the second wave may be produced as a result of the change in the nature of the product from the first reduction stage with increase in the electric field strength close to the electrode. In principle, this change may also take place without visible transformation of the polarogram. Thus the study of the mechanism of the reduction of complex organic compounds should combine a study of the nature of the influence of many factors with an analysis of the products obtained (see for example Refs. 84 and 85).

A number of papers have been devoted to a more detailed study of the action of proton donors on the reduction of aromatic compounds in an aprotic medium. Schwabe and Schmidt[36] found that when water is added to a dioxan solution of anthracene, fluorene, and pyrene, the first one-electron wave increases at the expense of the second, so that when the concentration of ethanol is sufficiently high, the polarogram shows only one two-electron wave.

Given and Peover[4,49,50] made a detailed study of the influence of various proton donors on the polarography of aromatic hydrocarbons and found that the most convenient proton donor is phenol, which is a sufficiently powerful donor, but which does not give a hydrogen liberation wave. Benzoic acid and HI are inconvenient, because in their solutions the hydrogen liberation waves mask the waves due to the reduction of the aromatic hydrocarbons. Acetic acid is used as an even stronger proton donor. The proton-donating properties of water are too weak, so that its action is appreciable only at high concentrations.

By analysing the form of the first wave for a number of aromatic compounds in the presence of a proton donor at concentrations sufficiently high for the first wave to be a two-electron wave, Given and Peover established that in DMFA the protonation is brought about by undissociated molecules of the proton donor (MA) and not by solvated protons. This conclusion cannot be regarded as proved for all proton donors used, however.

The nature of the action of proton donors depends on the nature of both the proton donor and the depolariser. Given and Peover distinguish various possibilities.

1. If the addition of the proton donor leads to the protonation of the anion-radical $R^{\cdot-}$ produced by attachment of the first electron, the first wave increases at the expense of the second until the latter disappears completely, since the radical $RH^{\cdot}$ is reduced more readily than the original molecule. Most aromatic hydrocarbons behave in this way.

2. If only the doubly-charged ion R^{2-} produced after the attachment of the second electron is protonated fairly rapidly, the first wave remains unchanged on the addition of the proton donor (the anion-radical $R^{\cdot-}$ is too weak a base), but the second is displaced towards less negative potentials. This behaviour is characteristic of quinones.

3. If the original molecule R is protonated, a new wave corresponding to the reduction of the protonated complex is produced in the range of less negative potentials. This behaviour is observed for aromatic carbonyl compounds.

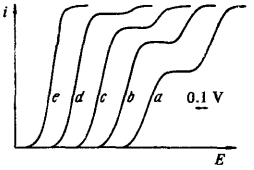


Figure 4. Influence of increase in the concentration of water on the polarogram for anthracene: *a*) 96% dioxan; *b*) 92% dioxan; *c*) 89% dioxan; *d*) 75% dioxan; *e*) 96% dioxan + 2×10^{-4} M HI (published data[25]).

4. The protonation of the doubly-charged anion makes more extensive (multi-electron) reduction possible. When the proton donor is added, the second wave is not only displaced towards less negative potentials but also undergoes an increase in height. Sometimes, additional waves appear. This behaviour is observed for pyrene, perylene, and phenanthrene.

5. If dimerisation of the radical-anions or radicals plays a significant part in the electrode process, a complex picture is observed on the introduction of proton donors. Sometimes, between the two original waves there appears a new wave, which increases with increase in the concentration of the proton donor at the expense of the second wave (benzaldehyde and xanthone in the presence of phenol).

This summary shows that experiments with the addition of proton donors in general do not contradict Hoijtink's scheme for the reduction of aromatic hydrocarbons. In fact, it may be considered that these experiments provide further important evidence in support of the scheme.

Grodza and Elving[56,86] tried to apply various criteria of classical polarography to the determination of the mechanism of the reduction of arylethylenes in ahydrous DMFA and in DMFA–water mixtures (80% or 90% DMFA). The experimental results for styrene, stilbene, 1,1-diphenylethylene, triphenylethylene, and tetraphenylethylene do not satisfy completely any of the postulated mechanisms. These authors consider, however, that the idea that the mechanism of the reduction changes along the polarographic wave corresponds most closely to the experimental results. At the foot of the wave, the reduction is preceded by protonation of the hydrocarbon molecule, whereas close to the limiting current plateau it is followed by protonation of the carbanions ($R^{\cdot-}$ or R^{2-}). Nevertheless, the mechanism involving preliminary protonation of the hydrocarbons in an aprotic medium can hardly be accepted. The authors themselves attribute their lack of success in attempts to

establish the mechanism reliably to the influence of the structure of the electrical double layer, for which it is difficult to allow.

Experiment indicates[87] that aprotic media show different efficiencies in increasing the difference in $E_{1/2}$ for the separate stages of the reduction (differentiating action). Thus for 9,10-anthraquinone and its derivatives in alkaline aqueous-alcoholic or aqueous-dioxan solutions, $\Delta E_{1/2}$ = 0.16–0.18 V; in acetonitrile in a supporting electrolyte of $(C_2H_5)_4NClO_4$, $\Delta E_{1/2} \simeq 0.5$ V; and in DMFA in the same supporting electrolyte, $\Delta E_{1/2} \simeq 0.7$ V. The phenomenon must undoubtedly be attributed to the difference in the rates of protonation of the carbanions. The magnitude of $\Delta E_{1/2}$ is influenced not only by the solvent, however, but also by the dissolved electrolyte. For example, for the same derivatives of 9,10-anthraquinone in DMFA in a supporting electrolyte of LiCl, $\Delta E_{1/2} = 0.30$ V, and in a supporting electrolyte of $(C_2H_5)_4NClO_4$, $\Delta E_{1/2} = 0.70$ V. It has been suggested that the influence of the electrolyte is also manifested in a displacement of the acid-base equilibrium, but it is of course not excluded that it is due to some extent to the influence of the change in the structure of the electrical double layer. Moreover, as shown by Peover and Davis[88], the association of the carbanions with the counter-ions of the electrolyte may have a significant influence. Ion association is responsible for the displacement of the wave towards less negative potentials, and the effect may be considerable. Thus for R^- the change from Li^+ to $(C_4H_9)_4N^+$ gives an effect of about 40 mV, whereas for R^{2-} it amounts to 300–600 mV. An even greater effect is produced by positive cations. For example, Nd^{3+} cations at a concentration of 2×10^{-3} M displaces the first wave for quinone by 550 mV, and the second by as much as 950 mV. Thus $\Delta E_{1/2}$ for the change from Li^+ to $(C_4H_9)_4N^+$, according to the data of Peover and Davis[88], decreases, whereas according to the data of Kheifets and Bezuglyi[87] it increases. The reason for the discrepancy in these result is not known.

The radical states postulated for the reduction of aromatic hydrocarbons have been studied many times by EPR spectroscopy[46,58,60]. It has been shown that the electrolysis of solutions of anthracene, anthraquinone, and benzophenone in an aprotic medium at the potentials of the limiting current of the first wave gives solutions with a high concentration of radical-anions[46]. The final products, however, were the dihydro-derivatives. This means that the radical-anions do not undergo dimerisation, but are protonated and undergo further electrochemical reduction. The radical-anions (unlike the radicals, whose EPR spectra are not recorded) are fairly stable, and although it is not stated in the works cited, their stability is undoubtedly due to the presence of the charge, which provides significant hindrance to both disproportionation and dimerisation.

In an elegant piece of work, Umemoto[60] used the EPR method to investigate the fate of the radical-anions in the bulk of the solution. The radicals were generated in an electrochemical cell, from which the solution was circulated along a capillary passing through the resonant cavity of the EPR spectrometer. The kinetics of the disappearance of the radical-anions were studied in the stationary solution (after the flow of solution through the capillary had stopped). The concentration of water was varied over a wide range (0–40%). The radical-anions in the bulk of the solution are protonated $R^- + H_2O \rightarrow RH^{\cdot} + OH^-$ and either are reduced at the electrode (if the radicals reach it, for example, in the cell) or remove an electron from another R^- radical-anion: $RH^{\cdot} + R^- \rightarrow RH^- + R$ (disproportionation). This reaction is possible since the $RH^{\cdot}$ radical has a greater electron affinity than the R^- radical-anion. Kinetic study showed that the reaction of the RH radicals with the R^- radical-anions is the only route by which the radical-anions disappear in the bulk of the solution.

III. REDUCTION IN STRONGLY ACIDIC MEDIUM

A solution of perylene in concentrated sulphuric acid shows absorption in the EPR spectrum similar to the absorption of a solution of the R^- radical-anion. The ultraviolet spectra of solutions of perylene in concentrated sulphuric acid and of its radical-anion in tetrahydrofuran[89] are also very similar. The suggestion that the radical-anions are formed in the sulphuric acid solutions is rejected on the basis of the fact that the reduction of perylene in these solutions corresponds to a polarographic wave for which $E_{1/2}$ is less negative by 0.5 V than $E_{1/2}$ for the triphenylcarbonium ion. Moreover, $E_{1/2}$ for the radical-anion of perylene (second wave for perylene) is more negative by 0.7 V than $E_{1/2}$ for the triphenylmethyl radical. Thus in solutions of perylene in sulphuric acid, singly-charged cations or the products of the attachment of protons (proton complexes) are formed[89].

Subsequent studies[90] showed that the proton complexes of aromatic hydrocarbons RH^+ in the presence of oxidising agents (oxygen, sulphuric acid, etc.) may be converted into R^+ cations, for example according to the reaction:

$$RH^+ + O_2 \rightarrow R^+ + HO_2^{\cdot} . \qquad (8)$$

If oxygen is removed from the solution, the hydrocarbon cations are slowly converted into proton complexes. The polarograms for solutions of perylene, tetracene, anthracene, and 3,4-benzpyrene in a mixture of trifluoroacetic acid and boron trifluoride, free from oxygen, each show two waves (Fig. 5)[91]. The first wave, lying in the range of negative potentials, is assigned to the reduction of hydrocarbon cations

$$R^+ + e \rightarrow R \qquad (9)$$

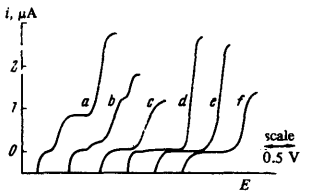


Figure 5. Polarograms for 10^{-3} M solutions of perylene (*a*), tetracene (*b*), anthracene (*c*), 3,4-benzpyrene (*d*), pyrene (*e*), and 1,2-benzanthracene (*f*) in $CF_3COOH + H_2O.BF_3$ (29 mole %) (published data[91]).

For the same concentrations of the hydrcarbons, the heights of the first waves differ considerably, due to the difference in the stabilities of the cations in the absence of oxygen. For this reason, the polarograms for pyrene and 1,2-benzanthracene do not show the first waves at all.

The second waves in most instances are twice as high as the first. This is observed particularly clearly in the polarograms for perylene, which is converted completely

into the cationic state. Thus the second wave is assigned to the two-electron reduction of the proton complexes RH^+:

$$R + H^+ \rightarrow RH^+ \quad (10)$$

$$RH^+ + e \rightarrow RH^\cdot \quad (11)$$

$$RH^\cdot + H^+ \rightarrow RH_2^{+\cdot} \quad (12)$$

$$RH_2^{+\cdot} + e \rightarrow RH_2 \quad (13)$$

From these studies it follows that the hydrocarbon cations are reduced more readily than the corresponding proton complexes. The proton complexes of hydrocarbons with linearly fused rings (anthracene, tetracene, and 1,2-benzanthracene) are reduced much more readily ($\Delta E_{1/2} \simeq 0.2$–$0.4$ V) than hydrocarbons with rings fused in angular fashion (pyrene, 3,4-benzpyrene, and perylene). It is suggested that the greater stability of the proton complexes of angular hydrocarbons to reduction is related to the more even distribution of the positive charge in the RH^+ cations of these hydrocarbons

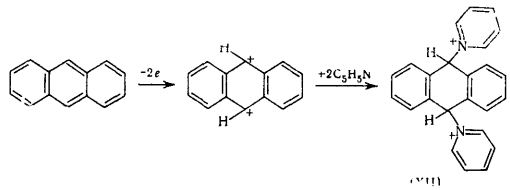
The electrolysis of a solution of perylene in trifluoroacetic acid containing a small quantity of H_2SO_4 (a relatively weakly oxidising medium) at the potentials of the limiting current of the first wave gave the original hydrocarbon—perylene[92]. This confirmed the suggestion that the first wave corresponds to the reduction of the R^+ cation.

IV. MECHANISM OF OXIDATION

The mechanism of the electrochemical oxidation of aromatic hydrocarbons has been studied by modern methods exclusively in an aprotic medium [62,77,93-105]. Either 0.1–2 M sodium perchlorate or 0.1 M tetraethylammonium perchlorate have been used as supporting electrolyte. Oxidation has been studied at vibrating[93,102], stationary[62,94,104], or rotating[77,95-97,99-101,103,105] platinum electrodes. Ag/Ag^+ or aqueous saturated calomel electrodes have been used as reference electrodes. With the latter, precautions were taken to prevent the entry of water into the solutions being studied.

Lund[93] found that a large number of aromatic hydrocarbons give normal or deformed oxidation waves, which he attributed to the removal of two electrons from the highest occupied molecular orbitals, the process involving only one benzene ring of the polynuclear hydrocarbon. Thus tetracene gives a second wave with approximately the same $E_{1/2}$ value as 5,12-dihydrotetracene, close to $E_{1/2}$ for a 2,3-dialkylnaphthalene. In lund's opinion, normal waves are given only by compounds for which the products of the two-electron oxidation are stable. For example, the product of the oxidation of indene, in Lund's opinion, is indane, that is a stable product, whereas the product of the oxidation of fluorene—presumably a derivative of dihydrofluorene—has a marked tendency to polymerise, so that the electrode is insulated from the solution by a layer of insoluble polymer. Other authors[77,96] also attribute the distortion of the waves to the adsorption of oxidation products on the electrode.

The removal of two electrons previously localised on one or two carbon atoms should lead to the formation of a doubly-charged carbonium cation. For example, for anthracene the charges are localised in positions 9 and 10. In the presence of electron donors such as pyridine, the doubly-charged cation is stabilised by the attachment of two molecules of the electron donor in the 9 and 10 positions:



(14)

(XII)

Preparative electrolysis of anthracene in acetonitrile in the presence of pyridine did in fact give 9,10-dihydroanthranyldipyridinium diperchlorate (XII). This compound contains only isolated benzene rings, so that it is not oxidised further (at the oxidation potential of anthracene). According to Lund's data, the $E_{1/2}$ values for the oxidation waves for aromatic alcohols[106] and the original aromatic hydrocarbons are very close, and on this basis he concluded that the first stage in the oxidation of the aromatic alcohols also involves the removal of two electrons from the aromatic rings.

The behaviour of aromatic hydrocarbons differs considerably for electrochemical reduction and oxidation. The attachment of a second electron takes place at a much more negative poential than that of the first, whereas in oxidation, two electrons are removed at the same potential. However, since the highest occupied and lowest vacant molecular orbitals in alternant hydrocarbons are positioned symmetrically with respect to the energy level of the atomic orbital (taken as zero), we should expect the aromatic hydrocarbons to show analogous behaviour during reduction and oxidation, that is successive removal or attachment of two electrons at significantly different potentials[77]. More distinct waves for the oxidation of aromatic hydrocarbons were obtained with a rotating indicator electrode[95,97] than with a vibrating electrode[93]. The electrolysis of anthracene in acetonitrile in the absence of pyridine gave the dimeric product bianthrone[98]. It has been possible to record the EPR spectra of the radical-cations produced in the oxidation of methoxybenzene[99] and 9-arylaminoanthracenes[105].

Study of the oxidation of aromatic hydrocarbons by cyclic volt-ammetry[62] showed that more positive $E_{1/2}$ values are obtained by using fast voltage sweeps than by using slow sweeps. The difference is attributed to the influence of conjugated chemical reactions of the radical-cations, which is felt when slow sweeps are used but not when fast sweeps are used. According to these results[62], the radical-cations are much less stable with respect to reaction with the solvent (their lifetime is of the order of several milliseconds) than the radical-anions produced during reduction.

According to the results[77] of the study of the oxidation of 60 hydrocarbons, the polarisation curves recorded by the classical polarograph give distinct first waves, whose slope (60–80 mV) corresponds to that for a reversible one-electron process. For *p*-phenylenediamine and its *N,N'*-tetramethyl derivative, alternating-current polarography showed a high degree of reversibility for both one-electron oxidations. Anilines give distinct one-electron waves, and also waves corresponding to further oxidation at more positive potentials. When pyridine is added, the first wave becomes a two-electron wave, probably as a result of an increase in the rate of the removal of a proton from the radical-cation. For dibenzanthracene, dibenzpyrene, 3,4-benzpyrene, and pyrene, the first waves are again one-electron waves. Other hydrocarbons give many-electron

waves; for example, the first wave for anthracene corresponds to the transfer of five electrons. In the work cited[77] various hydrocarbons were also studied by cyclic volt-ammetry with a stationary platinum electrode. The radical-cations of different hydrocarbons have different stabilities. Thus 9,10-dimethylanthracene at a rate of change of potential equal to 10–20 V min^{-1} shows a peak corresponding to the reduction of the radical-cation. The doubly-charged cation is even less stable. The radical-cation of anthracene is less stable than that of its 9,10-dimethyl derivative. The oxidation products of 1,2,5,6-dibenzanthracene are very unstable. Many-electron waves are observed when the product of the subsequent transformation of a very unstable radical-cation, which is produced by removal of the first electron, can undergo further oxidation at the potential of formation of the radical-cation. These results show that the removal of two electrons produces the same situation as the attachment of electrons: the successive removal of two electrons, sometimes complicated by chemical transformation of the radical-cation.

The radical-cations of aromatic hydrocarbons are more stable in methylene chloride than in acetonitrile[104]. For 9,10-diphenylanthracene, rubrene, and 1,3,6,8-tetraphenylpyrene, cyclic volt-ammetry with a stationary electrode has shown completely reversible one-electron processes, whereas for tetracene and anthracene, rapid chemical reactions take place under these conditions.

In the preceding section of this review it was shown that in strongly acidic media (concentrated sulphuric acid or a mixture of trifluoroacetic acid and boron trifluoride) the radical-cations of various hydrocarbons are fairly stable. The stability is apparently due to the difficulty of removing a proton from the radical-cation in strongly acidic media. From this it may be concluded that in aprotic solvents the low stability of the radical-cations is probably due to the possibility of proton removal

$$M^{\cdot+} \rightarrow R^{\cdot} + H^{+} \qquad (15)$$

The radicals formed may undergo subsequent reactions (dimerisation, disproportionation, oxidation). The study of the stages involved in the oxidation of aromatic hydrocarbons may apparently be more successful in strongly acidic than in aprotic media. If the reaction

$$R^{\cdot+} + e \rightarrow R \qquad (9)$$

studied in strongly acidic media, and

$$R \rightarrow R^{\cdot+} + e \qquad (16)$$

studied in aprotic media, are completely reversible, the $E_{1/2}$ values of the corresponding waves should be the same. Unfortunately, the $E_{1/2}$ values can be compared only very roughly, since the $E_{1/2}$ values for reaction (9) in strongly acidic media were measured either relative to the mercury bottom[92] or relative to the potential of the start of the dissolution of mercury[91], whereas the $E_{1/2}$ values for reaction (16) in aprotic media were measured either relative to an Ag/Ag^{+} reference electrode (with fast potential pulses)[62] or relative to an aqueous saturated calomel electrode (with slow potential pulses)[77]. The errors become even greater due to neglect of the interphase potentials. The difference in the $E_{1/2}$ values is greater than the maximum possible errors, however. Thus for perylene, according to a rough estimate, $E_{1/2}$ (sat. cal. el.) is +0.1V for reaction (9) and +1.04 V for reaction (16). This discrepancy is possibly due to the fact that the processes taking place are actually more complex than at present assumed.

From the foregoing it follows that for an exact comparison of the $E_{1/2}$ values of oxidation with other molecular parameters it is necessary to determine $E_{1/2}$ by cyclic volt-ammetry with fast potential pulses, as in Ref. 62.

V. CORRELATION OF THE VALUES OF THE HALF-WAVE POTENTIALS

At the present time, in the polarography of aromatic and unsaturated hydrocarbons, extensive use is made of correlations between the values of the half-wave potentials and various molecular constants. The most important of these is undoubtedly the correlation of the half-wave potentials with the energies of molecular orbitals. This has made possible a fairly rigorous verification of the conclusions reached by applying quantum-chemical calculations to the molecules of aromatic and unsaturated hydrocarbons. It has been correctly noted[107] that the application of correlation relations makes it possible to predict $E_{1/2}$ values for compounds which have not been studied, and also to find molecular parameters which are not readily obtainable by other methods, such as ionisation potentials and electron affinities. Thus the study of correlation relations is stimulating further experimental and theoretical studies in this field.

Correlations are most successful when the mechanism of reduction or oxidation is the same for the series of compounds being considered and particularly when these processes are reversible. This last feature is necessary for the application of the relationships for thermodynamically reversible processes.

The idea forming the basis of the correlation of $E_{1/2}$ with the energies of molecular orbitals was formulated by Maccoll[64], who extended to the electrochemical reduction of aromatic hydrocarbons Hückel's concept of the relationship between the energy of the lowest vacant molecular orbital and the ease of attachment of alkali metals to aromatic hydrocarbons. In both instances, one or two electrons (from the alkali metal or the electrode) are transferred to the lowest vacant antibonding molecular orbital. The reversible reduction potential is related to the changes in enthalpy (ΔH) and entropy (ΔS) by the familiar relationship

$$nFE_0 \quad \Delta H - T\Delta S \,. \qquad (17)$$

It is subsequently pointed out that ΔH depends on the energy required for the transfer of one or two electrons to the lowest vacant orbital, that is it is related to the coefficient a_{n+1} in the expression for the energy of the lowest vacant orbital. Comparison of the $E_{1/2}$ values found by Wawzonek and Laitinen[13,14] with the coefficients a_{n+1} calculated by the simple Hückel molecular orbital method (Fig. 6) showed a fairly good linear relationship between these quantities.

This idea was used by Lyons[108] to predict the influence of substituents on the value of $E_{1/2}$ by calculating the change in the energy of the lowest vacant molecular orbital on introduction of the substituent. If the energy of the lowest vacant molecular orbital is increased, reduction is made more difficult, and vice versa. For example, for the introduction of a methyl group into the pyridine ring, theory predicts a displacement of $E_{1/2}$ by 30 mV towards more negative potentials.

Pullman and coworkers[109] verified the correlation of $E_{1/2}$ with a_{n+1} for a large number of compounds (alternant aromatic hydrocarbons and unsaturated compounds). It was found that the plot of $E_{1/2}$ against a_{n+1} cannot be represented by a single straight line for all groups of com-

pound. The linear relationship is observed most rigorously for condensed benzenoid hydrocarbons. Linear condensation of the benzene rings leads to a decrease in a_{n+1} and to an increase in the ease of reduction. The easier reduction of anthracene compared with phenanthrene indicates that the energy of the lowest vacant orbital is greater in phenanthrene. This correlation predicts that for benzene the half-wave potential should be about -3.6 V, This explains why benzene cannot be reduced by direct transfer, whereas reduction by the most active alkali metal—lithium—takes place when it is produced electrochemically[44,110]. The data of phenylethylenes and phenylacetylenes do not fall within the $E_{1/2}$–a_{n+1} correlation for benzenoid hydrocarbons[109]. They lie on an independent straight line, with the exception of the results for tetraphenylethylene. The deviation of this group of compounds from the general straight line is related[109] to the limited accuracy of the calculation of a_{n+1}.

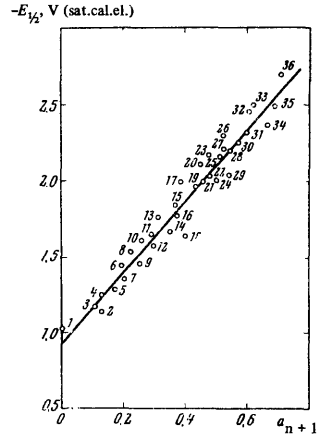


Figure 6. Dependence of the half-wave potentials (in aqueous dioxan) on the coefficient a_{n+1}: *1*) triphenylmethyl; *2*) 1,4-dibiphenylenebutadiene; *3*) 1,6-dibiphenylenehexatriene; *4*) 1-phenyl-12-biphenylenedodecahexaene; *5*) 1-phenyl-8-biphenyleneoctatetraene; *6*) 1,12-diphenyldodecahexaene; *7*) 1-phenyl-6-biphenylenehexatriene; *8*) 1,10-diphenyldecapentaene; *9*) 1-phenyl-4-biphenylenebutadiene; *10*) 1,8-diphenyloctatetraene; *11*) acenaphthylene; *12*) anthanthrene; *13*) 1,6-diphenylhexatriene; *14*) perylene; *15*) 1,2-benzpyrene; *16*) fluoranthene; *17*) 1,4-diphenylbutadiene; *18*) azulene; *19*) anthracene; *20*) pyrene; *21*) 1,2-benzanthracene; *22*) 1,2,5,6-dibenzanthracene; *23*) 1-phenylbutadiene; *24*) 4,5-benzpyrene; *25*) stilbene; *26*) chrysene; *27*) 2,2′-binaphthyl; *28*) quaterphenyl; *29*) coronene: *30*) 1,1-diphenylethylene; *31*) terphenyl; *32*) phenanthrene; *33*) naphthalene; *34*) styrene; *35*) triphenylene; *36*) biphenyl (published data[2]).

The fact that tetraphenylethylene does not fall within the correlation for the unsaturated compounds is tentatively attributed to the non-coplanarity of this compound, as a result of which the conjugation is is weakened, the lowest vacant orbital is raised, and the reduction is made more difficult. Other authors[27,31,82,111,112] have also drawn attention to the part played by coplanarity. Thus according to Hoijtink's data[27], the molecules of such aromatic hydrocarbons as 9,9′-bianthryl, rubrene, and 1,1′-binaphthyl are also non-coplanar, their structure being much closer to one in which the separate parts of the molecule joined by simple C–C bonds are mutually perpendicular, since the $E_{1/2}$ values almost coincide with those for anthracene, tetracene, and naphthalene. The effect of departure from coplanarity in the arylethylene series has been studied in more detail. Pointeau and de Villepin[111] calculated the dependence of the energy of the lowest vacant orbital for biphenyl derivatives on the angle between the planes of the two rings and compared the results with experimental measurements. In the calculations it was assumed that the energy of the orbital is a sinusoidal function of the angle between the rings. The calculation showed that even fairly marked departure from coplanarity gives a scarcely perceptible effect. Thus for rotation of the rings through 20° we should expect a change in $E_{1/2}$ by only 40 mV. The departure from coplanarity was brought about by the introduction of substituents into the ortho-position. The expected effect could not be detected, however, since it was masked by the effects of the substituents.

The effect of the departure from coplanarity is also revealed[82] by comparing the $E_{1/2}$ values for two aromatic compounds with the same number of benzene rings, of which one is condensed, so that the molecule must be planar, whereas the molecule of the other contains a simple C–C bond, about which rotation of sections of the molecule can take place. It is true that the molecules of these compounds also differ in the number of π electrons, so that the effect of coplanarity cannot be established in pure form. Nevertheless, this comparison is useful. Thus $E_{1/2}$ for naphthalene is less negative by 95 mV than $E_{1/2}$ for biphenyl; for anthracene and terphenyl, $\Delta E_{1/2} = 445$ mV, and for tetracene and quaterphenyl, $\Delta E_{1/2} = 630$ mV. The values of $E_{1/2}$ were taken from Bergman's papers[39,40].

Phenylacetylenes are less readily reduced than phenylethylenes[109]. This phenomenon is due to the greater localisation of electrons on the triple bond and the consequent raising of the lowest vacant orbital.

A detailed derivation of the relationship between $E_{1/2}$ and a_{n+1} was first tiven by Hoijtink and van Schooten[22].

For the change in free energy for the attachment of an electron to a conjugated molecule R, which is related to the reduction potential by Eqn. (17), we can write

$$\Delta G^0 = [\mu^0_R]_{aq} + [\mu^0_{el}]_{Hg} - [\mu^0_{R^-}]_{aq} \qquad (18)$$

where $[\mu^0_R]_{aq}$ and $[\mu^0_{R^-}]_{aq}$ are the chemical potentials of the molecule R and the radical-anion R^- in solution, and $[\mu^0_{el}]_{Hg}$ the chemical potential of the electron in mercury. Eqn. (18) transforms into

$$\Delta G^0 = [\mu^0_R]_g + [\mu^0_{el}]_{Hg} - [\mu^0_{R^-}]_g + [\Delta G^0]_{solv} \qquad (19)$$

where the subscript "g" denotes the gaseous state, and $[\Delta G^0]_{solv}$ is the change in ΔG^0 resulting from the solvation of R and R^-. $[\mu^0_R]_g - [\mu^0_{R^-}]_g$ is equal to the electron affinity of the molecule R in the gaseous state (A). Thus

$$\Delta G^0 = A + [\mu^0_{el}]_{Hg} + [\Delta G^0]_{solv} \qquad (20)$$

But,

$$E = E_0 + \frac{RT}{F} \ln \frac{C_R}{C_{R^-}} = E_{1/2} + \frac{RT}{F} \ln \frac{(i_d - i)}{i} \qquad (21)$$

$$E_0 = \frac{\Delta G^0}{F} = E_{1/2} + \frac{RT}{F} \ln \frac{D_R^{1/2}}{D_{R^-}^{1/2}} \qquad (22)$$

From Eqns. (20) and (22) we have

$$A = FE_{1/2} + RT \ln \frac{D_R^{1/2}}{D_{R^-}^{1/2}} - [\mu_{el}^0]_{Hg} - [\Delta G^0]_{solv} . \quad (23)$$

To the first approximation it may be assumed that $\lg (D_R/D_{R^-})^{1/2}$ and $[\Delta G^0]_{solv}$ are the same for the compounds being considered. We then have

$$A = FE_{1/2} + C . \quad (24)$$

The electron affinity is equal to the negative value of the energy of the lowest vacant orbital $(n + 1)$:

$$\varepsilon = \alpha - a_{i+1}\beta \quad (25)$$

where α is the energy of a π electron localised on an individual carbon atom, β the exchange integral for two neighbouring carbon atoms, and a_{n+1} the numerical coefficient obtained by solving the secular equation in the method of molecular orbitals. Thus

$$-\alpha + a_{n+1}\beta = FE_{1/2} + C . \quad (26)$$

The constants α and C are eliminated by writing the difference for the two compounds:

$$\begin{gathered} -\alpha + a_{i-1}\beta = FE_{1/2} + C \\ -\alpha + a'_{i+1}\beta = FE'_{1/2} + C \\ \hline (a_{n+1} - a'_{n+1})\beta = (E_{1/2} - E'_{1/2})F \end{gathered}$$

or in electron-volts

$$(a_{n+1} - a'_{n+1})\beta = E_{1/2} - E'_{1/2} \quad (27)$$

As standard, it is convenient to take the triphenylmethyl radical, for which $\varepsilon = \alpha$ $(a_{n+1} = 0)$ and $E'_{1/2} = -1.05$ V. By substituting these values in Eqn. (27) we obtain the final expression

$$E_{1/2} = a_{n+1}\beta - 1.05 \quad (7)$$

previously given in the first section.

It can be seen from the discussion that Eqn. (7) is approximate, since assumptions known to be inaccurate were made in its derivation. The change in $\ln (D_R/D_{R^-})^{1/2}$ and $[\Delta G^0]_{solv}$ on going from one compound to another with similar structure, however, is also apparently monotonic, so that $E_{1/2}$ still remains an approximately linear function of a_{n+1}.

Subsequently, attempts were made to analyse the experimental data on the basis of more accurate relationships[113,114]. This gave nothing fundamentally new, however. Moreover, the simple relationship (7) has proved satisfactory. It has been verified many times[22,23,27,29,30,37,52,67,115-121]. Without giving details of these papers, we would point out that a satisfactory correlation is also obtained under experimental conditions in which the reduction is not completely reversible (75% dioxan), apparently because the irreversibility resulting from protonation of the radical-anions has little influence on the value of $E_{1/2}$. When comparing $E_{1/2}$ values it is best to use experimental data obtained under identical experimental conditions, since even apparently insignificant changes in the conditions of the experiment may have a significant influence on the $E_{1/2}$ values, through change in the potential of the reference electrode or diffusion potentials, or through the radical-anions forming ion pairs[88,114] with the counter-ion of the supporting electrolyte.

The correlation given by Eqn. (7) covers not only alternant aromatic hydrocarbons, but also the non-alternant azulene. Azulene, however, shows appreciable departure from this correlation. Thus according to the calculation, $E_{1/2} = -1.87$ V[65] whereas experiment gives $E_{1/2} = -1.64$ V[65]. Various suggestions have been put forward to explain this anomaly. In Hoijtink's opinion[27], this phenomenon cannot be due to the fact that in the approximate calculation by the molecular orbital method used, all the bond lengths in the azulene molecule were taken as equal, since a more rigorous treatment making allowance for the difference in the bond lengths leads to an even greater discrepancy. Hoijtink suggested that the increased ease of reduction of azulene is due to decreased strain of the rings in the azulene molecule when it loses an electron.

In Streitwieser's opinion[2], the correlation can be improved by using a higher value of β for the 9,10 bond (common to both rings).

An even more striking difference between the $E_{1/2}$ values predicted on the basis of correlation (7) and the experimental values is observed for charged non-alternant hydrocarbons—the tropylium and azulenium cations. For these compounds the discrepancy in the $E_{1/2}$ values reached 1.4–1.5 V.

It has been suggested[122] that this anomaly is due to the polarity of the molecules of non-alternant hydrocarbons, leading to a change in the solvation energies of the reacting species and in the electron affinities. For example, on going from the reduction of benzene to the reduction of the tropylium cation these quantities change as follows. Preferential solvation of the product (the R^- radical-anion) is replaced by preferential solvation of the starting material (the tropylium cation). The difference in the solvation energies for these two reactions is about 4 eV, the reduction of the tropylium cation becoming more difficult as a result of the change in the solvation of the components. This effect is masked, however, by the effect of the increased electron affinity of the tropylium cation (by more than 6 eV compared with benzene).

The correlation (7) can be extended to non-alternant hydrocarbons by the introduction of a term allowing for the polarity of the molecule

$$E_{1/2} = a_{n+1}\beta - E^0_{1/2} + kq_r \quad (28)$$

where q_r is the maximal positive charge on a carbon atom of the molecule.

The rule formulated by Hoijtink, according to which the radical RH· of an aromatic hydrocarbon is always reduced more readily than the original hydrocarbon R, may not apply for a non-alternant hydrocarbon, because of the effect of the polarity of the molecule. For this reason, apparently, azulene is reduced more readily than the RH· radical of azulene.

The problem of a possible correlation of the $E_{1/2}$ values of aromatic hydrocarbons with the para-localisation energies has been widely discussed[123-130]. The discussion was initiated by Basu and Bhattacharya[123], who, on the basis of the data of Wawzonek and Laitinen[14] obtained with solutions in 75% dioxan, indicated for the first time the possibility of a correlation between $E_{1/2}$ and the energy of localisation of two electrons in the para-position of the hydrocarbon. A basis for this conclusion was provided by the fact that in 75% dioxan the first wave corresponds to the transfer of two electrons, and reduction generally takes place in the para-position. In fact, they found a satisfactory linear relationship between the $E_{1/2}$ values and the para-localisation energies. Serious objections were raised to this work, however. Pullman and Pullman[124] corrected various para-localisation energy values, and the correlation with $E_{1/2}$ was thereby destroyed. They also pointed out that reduction does not always involve the para-position, and the absence of a linear relationship was demonstrated for a large number of examples. For example, the energy of

para-localisation in polyphenyls remains approximately constant with increase in the number of benzene rings, whereas $E_{1/2}$ becomes less negative. Pullman and Pullman point out that the parallelism sometimes observed between $E_{1/2}$ and the para-localisation energy is possibly due to the fact that the localisation (polarisation) energy is often revealed in the energy of the first vacant orbital. Given's objections [127] reduce to the fact that since in the reduction of aromatic hydrocarbons, two electrons are in fact transferred in stages, the energy of para-localisation is not related to the least negative $E_{1/2}$. It is more correct to expect a correlation of $E_{1/2}$ with the energy of localisation of an electron in an individual position, and this correlation is in fact satisfactory [127]. At present, the correlation of the $E_{1/2}$ values with the para-localisation energies has not been accepted.

By analogy with the correlation of $E_{1/2}$ for the waves for the reduction of aromatic hydrocarbons with the root a_{n+1} of the Hückel secular equation for the first vacant molecular orbital, a correlation was found between $E_{1/2}$ for the oxidation waves and the root a_n for the highest filled bonding orbital [131]. The experimental values of $E_{1/2}$ for oxidation were taken from Lund's paper [93]. A satisfactory correlation was observed (Fig. 7), despite the fact that the waves corresponded to a two-electron oxidation, and, as shown later [62], this oxidation takes place irreversibly because of subsequent rapid transformation of the radical-cations.

Figure 7. Plot of $(E_{1/2})_{ox}$ against a_n for alternant hydrocarbons (circles) and fluoranthene (triangle) (published data [131]).

Since for alternant hydrocarbons the vacant and occupied orbitals are positioned symmetrically with respect to the atomic orbital, that is $a_n = -a_{n+1}$, there is a linear relationship between $E_{1/2}$ for the oxidation and $E_{1/2}$ for the reduction of alternant hydrocarbons [131]. This correlation is important, because it makes it possible to investigate the characteristic features of the behaviour of non-alternant hydrocarbons, which depart even further from this correlation (Fig. 8) than from the linear relationship between $E_{1/2}$ for the reduction or oxidation and a_{n+1} or a_n.

The values of $E_{1/2}$ for the reduction waves have been used to find the electron affinities of the molecules of aromatic hydrocarbons, which are identified with the energies of the first vacant orbital. This possibility was first examined by Lyons [132]. We shall take the derivation of the relationship between $E_{1/2}$ and the electron affinity (A) from Matsen's paper [133].

The electrode processes in the measurement of $E_{1/2}$ for reduction, relative to a saturated calomel electrode, are arbitrarily broken down into the following stages:

$$R_g + e_g \rightarrow R_g^- + A \quad (29)$$

$$R_{soln} + R_g^- \rightarrow R_g + R_{soln}^- + \Delta G^0_{solv} \quad (30)$$

$$e\,(Hg) \rightarrow e_g - 4.54\ eV\ (work\ function) \quad (31)$$

$$Hg_{liq} + Cl^-\ (sat.aq.) \rightarrow (HgCl)_{solid} + e\,(Hg) - 0.56\ eV \quad (32)$$

$$Cl^-\ (sat.aq.) \rightarrow Cl^-\ (sat.aq) + 0.03\ eV \quad (33)$$

$$R_{soln} + Hg_{liq} + Cl^-\ (sat.aq) \rightarrow R^-_{soln.} + HgCl_{solid} \quad (34)$$

$$E_{1/2} = A + \Delta G^0_{solv} - 5.07 \equiv A' - 5.07\ (eV) \quad (35)$$

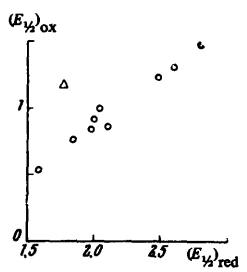


Figure 8. Plot of $(E_{1/2})_{ox}$ against $(E_{1/2})_{red}$ (published data [131]).

The difference in the free energy of solvation ΔG^0_{solv} is determined chiefly by the free energy of solvation of the ion, and can be calculated by means of the Born equation

$$\Delta G^0_{solv} \simeq 27.2\left(1 - \frac{1}{D}\right)\frac{a_0}{\bar{r}}\ (eV), \quad (36)$$

where $\bar{r}$ is the mean radius of the ion, a_0 the Bohr radius, and D the dielectric constant. In a first approximation, $\bar{r}$ is proportional to the cube root of the number of benzene rings in the molecule (p). Thus as $p \rightarrow \infty$ (graphite), $\Delta G^0_{solv} \rightarrow 0$ and $A' \rightarrow A$.

Since a linear relationship exists between $E_{1/2}$ and a_{n+1}, a linear relationship should exist between A' and a_{n+1}. This linear relationship is in fact observed (Fig. 9). Extrapolation of the straight line obtained by plotting A' against a_{n+1} to $a_{n+1} = 0$ (graphite) gave A for graphite (3.8 eV). From this it follows that for graphite $E_{1/2} = -1.27$ V. This value is obviously too negative. Other methods give for graphite $A = 4.39$ eV ($E_{1/2} = -0.68$ V). Finally, from the correlation between the values of A and the spectroscopic characteristics, we have for graphite $A = 4.8$ eV ($E_{1/2} = -0.27$ V). Direct measurements of the reduction potentials of graphite have not been made, but in this connection it may be mentioned that the low current efficiencies in the reduction of benzene by metallic lithium generated electrolytically on graphite were attributed to the partial utilisation of electricity for the hydrogenation of graphite [44]. This suggestion is confirmed by the marked erosion of the graphite cathode, in contrast to the behaviour of a carbon cathode [134].

If the values of A are calculated, it is possible, by comparing them with the $E_{1/2}$ values, to estimate the solvation energy ΔG^0_{solv}. [135] It was established in this way that ΔG^0_{solv} generally decreases with increase in the number of

benzene rings in the molecule of an aromatic compound. For the estimation of the solvation energies, the measurement of the electron affinities of the molecules in the gaseous phase is of considerable importance. Wentworth and Becker[136] suggested a method based on the measurement of the equilibrium constants for the capture of thermal electrons by the gaseous molecules in a gas-chromatographic detector, and observed a good correspondence between the values of A and $E_{1/2}$.

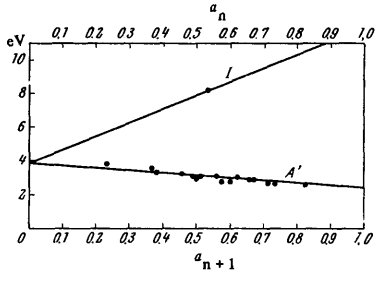


Figure 9. Dependence of the ionisation potential (I) on the energy of the highest filled orbital (the coefficient a_n) and of the apparent electron affinity (A') on the energy of the lowest vacant orbital (the coefficient a_{n+1}) for a number of hydrocarbons with condensed rings (published data[133]).

10)[137]. It has been the subject of a large number of studies[33,39,40,84,93,96,97,99,100,102,109,112,119,138-140]. The slope of the straight line obtained by plotting $E_{1/2}$ against E_ν should be equal to two. A bathochromic shift of the long-wave absorption band (that is towards longer wavelengths) corresponds to a decrease in the difference between the energies of the two orbitals, and a hypsochromic shift corresponds to an increase.

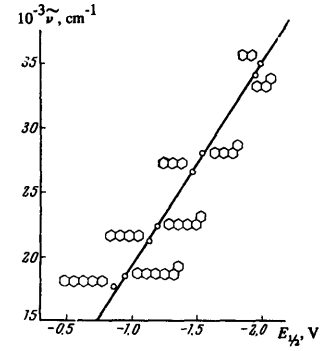


Figure 10. Plot of $\tilde{\nu}$, cm^{-1} against $E_{1/2}$ for the reduction of cata-condensed aromatic hydrocarbons in cellosolve ($\tilde{\nu}$ is the wave number of the p-band in the absorption spectrum) (published data[39]).

The $E_{1/2}$ values for the anodic oxidation waves are used[133] to determine ionisation potentials (I), that is the energies required to remove the least firmly bound electron (to remove an electron from the highest occupied orbital), so that the ionisation potential is equal to the energy of a π electron in this orbital and is an important characteristic of molecules. For graphite, $a_n = a_{n+1} = 0$ and $\Delta G^0_{solv} = 0$ and $A = 1$. Theory predicts that for alternant hydrocarbons the ionisation potential and electron affinity should be symmetric with respect to the work function of graphite (A).

We have seen that the $E_{1/2}$ values for reduction and oxidation contain information on the energy levels of molecules with generalised π electron systems. The same information is carried in the absorption spectra, so that a relationship should exist between the $E_{1/2}$ values and the spectroscopic characteristics of aromatic hydrocarbons. Watson and Matsen[137] were the first to draw attention to this relationship. On absorption of light energy the molecule is excited, and this is reflected in the transfer of an electron from one of the occupied orbitals to a higher vacant orbital. The lowest-energy transfer in the ground state of a molecule takes place from the first occupied orbital to the lowest vacant orbital. For alternant hydrocarbons, $a_n = -a_{n+1}$ and for the energies of the orbitals being considered we can write $\alpha + a_n\beta$ and $\alpha - a_{n+1}\beta$. The difference between the energies of these two orbitals, equal to the excitation energy $h\nu$, is

$$h\nu = -(a_n + a_{n+1})\beta = -2a\beta \quad . \qquad (37)$$

Since there is a linear relationship between a_{n+1} and $E_{1/2}$, there should be a linear relationship between $E_{1/2}$ and the frequency of the absorption band with longest wavelength. This correlation has in fact been observed (Fig.

Attempts have been made to correlate the $E_{1/2}$ values with various other properties of molecules. Thus a correlation has been noted between $E_{1/2}$ and the relative adsorbability of conjugated hydrocarbons on alumina[141]. It has been suggested that the $E_{1/2}$ values for the reduction of vinyl monomers change in the same sense as the ability of the monomer to undergo anionic polymerisation[29,30]. A parallelism has been noted between $E_{1/2}$ for the reduction of aromatic hydrocarbons and their thermal stability[142]. The $E_{1/2}$ values also show a correlation with the values of the g-factor in the EPR spectra of the radical-ions of alternant hydrocarbons[143,144]. The $E_{1/2}$ values have been compared with the carcinogenic activity of aromatic hydrocarbons[118,145]. In the last instance the regularity is not clear. Most carcinogenic substances exhibit both electron-donating and electron-accepting properties, but these functions are less marked for non-carcinogenic compounds[145].

VI. CHARACTERISTIC FEATURES OF THE ADSORPTION OF BENZENOID AROMATIC HYDROCARBONS

The specific electronic structure is also reflected in the adsorption characteristics of aromatic hydrocarbons[146]. Even in early papers it was noted that aromatic compounds are adsorbed much more readily at the mercury–solution boundary than at the free surface of the solution, the electrocapillary maximum being displaced in the cathodic direction[147,148]. The studies dealt chiefly with the hydroxy- and amino-derivatives, so that these experimental facts were interpreted as the result of an intensification of the interaction of the oxygen and nitrogen atoms of the hydroxy- and amino-groups with mercury, because of the flatter orientation of the benzene rings in the adsorbed layer on

mercury. Detailed measurements of the electrocapillary curves in solutions of unsubstituted condensed aromatic hydrocarbons by Gerovich[149-153] show, however, that unsubstituted non-polar aromatic hydrocarbons also displace the maximum of the electrocapillary curve towards more negative values and are preferentially adsorbed on the positively charged surface of the mercury electrode. This suggested that the observed anomalies are related to the adsorption characteristics of the aromatic rings themselves, and not of the polar substituents. In fact, the adsorbability of aromatic hydrocarbons on a positively charged surface increases in the order: benzene, naphthalene, phenanthrene, that is with increase in the number of benzene rings. On the other hand, hydrogenated benzene and naphthalene (cyclohexane and decalin) are adsorbed preferentially on a negatively charged mercury surface and displace the maximum of the electrocapillary curve in the anodic direction, which is characteristic of the adsorption of aromatic compounds[151].

It has been suggested that in the adsorption of aromatic hydrocarbons on a positively charged mercury surface an important part is played by the interaction of the system of π electrons of the hydrocarbon molecule with the positive charges of the mercury surface, with partial transfer of positive charge to the aromatic ring. This interaction is possible only with planar orientation of the molecules of the aromatic hydrocarbons in the adsorbed state. Calculation of the limiting adsorption (Γ_∞) for benzene, naphthalene, and phenanthrene on mercury from electrocapillary measurements showed that with increase in the number of benzene rings, Γ_∞ decreases, so that the area corresponding to one molecule of adsorbate increases[152]. This also confirmed the assumption regarding the flat orientation of the molecules of the adsorbed aromatic hydrocarbons.

Proof of the specific behaviour of aromatic hydrocarbons during adsorption on mercury is also found in work by Blomgren and coworkers[154], in which the dependence of the adsorbability of organic compounds on the solvation energy (solubility) was studied for a large number of substances. Aromatic compounds fall outside the established relationship, and this is again interpreted as due to the influence of the π electronic interaction of the molecules of these compounds with the mercury surface.

This interaction is so marked that it is not eliminated completely when a positive charge is introduced into the molecule of an aromatic hydrocarbon. For example, on going from aniline (neutral medium) to the anilinium cation (acid medium) the adsorption for positive charges on the surface is weakened considerably as a result of electrostatic repulsion but is not eliminated completely[155,156], and the quantity absorbed is almost independent of the potential of the electrode over a fairly wide range (~ 1 V).[157]

Gerovich[151] suggested that the formation of an adsorption layer of aromatic hydrocarbon molecules orientated parallel to the mercury surface should not be accompanied by marked changes in capacity. This suggestion was supported by the fact that the slope of the ascending branches of the experimental electrocapillary curves for solutions of aromatic hydrocarbons are almost the same as those for the solutions of the indifferent electrolyte (Fig. 11).

Direct measurements of the differential capacity showed that for the most positive charges on the surface the differential capacity in solutions of the indifferent electrolyte and the aromatic hydrocarbon coincide[158]. Moreover, in acidic solutions of aniline, from which adsorption of the anilinium cation takes place, the curves obtained by plotting C against E coincide throughout the entire range of potentials[159]. The calculated C–E curves do not coincide with the experimental curves in the range of positive charges on the surface, because of neglect of the π electronic interaction[160,161]. If the hydrogen atoms in the molecules of the aromatic compounds are replaced by fluorine atoms with high electron affinity, the π electron interaction is weakened to such an extent that it is not a decisive factor in the adsorption on mercury[162,163].

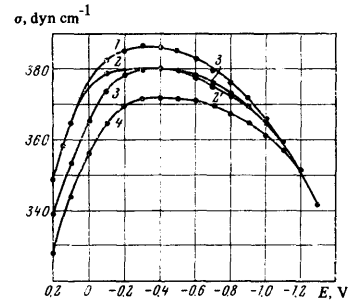


Figure 11. Electrocapillary curves for an aromatic hydrocarbon (naphthalene) in ethanol: *1*) ethanol + 0.1 M NH_4NO_3; *2*) 0.3 M decalin; *3*) 0.05 M naphthalene; *4*) 0.3 M naphthalene (published data[151]).

Under certain conditions the C–E curves for aromatic hydrocarbons, for positive charges on the surface, show peaks, which, however, do not correspond to the adsorption–desorption process (unlike the cathodic peaks). The production of these peaks is related to the re-orientation of the molecules of the aromatic hydrocarbon, that is to the change from a flat orientation for positive charges on the surface to an orientation close to vertical for negative charges on the surface[158,160]. This phenomenon was not detected by a less sensitive method for measuring electrocapillary curves.

The ideas put forward here have been used in an examination of the adsorption of aromatic hydrocarbons on other metals: cadmium[164], gold[165], iron, nickel, copper, and platinum[166]. The study of the characteristic features of the adsorption of organic compounds on metals may be useful in the detection of aromatic properties[167].

In conclusion is should be noted that work on the polarography of aromatic hydrocarbons has had a marked influence on the entire field of the polarography of organic compounds. At the present time, in the study of the mechanism of the reduction of organic compounds, extensive use is made of aprotic media for breaking down multistage processes into individual stages and for revealing the reversible elementary stages; the effect of the addition of proton donors to aprotic media is used to determine the basic nature of the original molecules, radicals, and radical-anions; alternating-current polarography makes it possible to verify more rigorously the reversibility of the electron-transfer stages and to measure the rate constants of these processes; the combination of polarography and EPR spectroscopy is finding application in the electrochemical preparation and study of the properties of radical species. In the study of the mechanism of the oxidation of organic compounds, use is made of experience gained in the study of the oxidation of aromatic hydrocarbons (the

use of acetonitrile as solvent, the rotating platinum microelectrode, and fast potential pulses). The determination of the correlational dependence of polarographic characteristics on molecular constants calculated by quantum-chemical methods has been widely applied.

A review of the published information on the polarography of aromatic hydrocarbons reveals various problems which have been insufficiently studied, and work on these problems should give most promising results.

1. Systematic studies of the path of the electrochemical reduction of various aromatic hydrocarbons and the role of the nature of the solvent and the indifferent electrolyte (the formation of ion pairs and complexes).

2. Deeper study of the mechanism of oxidation of aromatic hydrocarbons.

3. Study of the mechanism of the reduction of aromatic hydrocarbons in strongly acidic media.

4. Study of the correlational relationships, particularly the anomalous relationships (non-alternant hydrocarbons, compounds whose molecules are non-coplanar, etc.) on the basis of more accurate quantum-chemical calculations

5. The development of a theory of the adsorption of aromatic hydrocarbons on metals.

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Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow

U. D. C. 541.124

Study of the Mechanism of Homolytic Reactions in Solution by a Combination of Isotopic and Mass-spectrometric Methods

I.P.Gragerov

The use of mass spectrometry for the isotopic analysis of the products of homolytic reactions in deuterated solvents has made is possible to find the ratio of all isotopic forms of the substances studied and has opened up new possibilities in the study of the mechanism of homolytic reactions.
The present review examines critically work carried out by this method. These studies have made it possible to investigate the properties and regular features of the behaviour of various kinds of hydrocarbon radical in various solvents; have led to the discovery of reliable criteria for distinguishing free-radical processes from homolytic reactions taking place in the reaction complex without the liberation of radicals; and have made possible a deeper study of the mechanism of a number of types of free-radical reaction—the photolysis of organic halides and their reactions with metals, the thermal decomposition of benzoyl peroxide, diazo-compounds, and azo-compounds, various reactions of organometallic compounds, and processes of hydrocarbon oxidation. The bibliography contains 144 references.

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I. INTRODUCTION

Since 1960, studies of the mechanism of homolytic reactions in solution by means of deuterium have been combined, on an increasing scale, with analysis of the products by low-voltage mass spectrometry. In this method (see for example Refs. 1 and 2), the ionising voltage in the mass spectrometer is reduced, so that the minimal number of fragment ions is formed. In a number of instances it is possible to obtain mass spectra corresponding to the molecular ions of isotopic forms of the compounds being analysed and to find the ratio of these forms directly from the ratio of the intensities of the corresponding peaks. These data have proved to be more valuable for an understanding of reaction mechanisms than previously available information on only the total concentration of deuterium in the products.

The considerable volume of work which has now been carried out by means of a combination of the isotopic and mass-spectrometric methods, and the importance of the results, have stimulated the publication of this review. The work examined in it has been directed towards the study of the properties of radicals with different structures, the investigation of the mechanism of a number of specific reactions with the intermediate formation (or assumed formation) of radicals, and the discovery of new criteria for distinguishing reactions involving free radicals from homolytic reactions taking place in the reactive complex. This last requires some explanation.

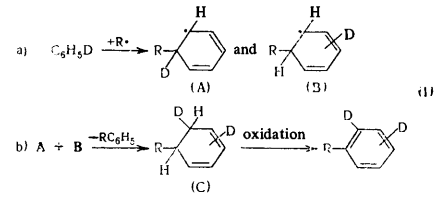
For any homolytic reaction in solution, mechanisms of two types are possible a priori—a free-radical mechanism and a mechanism which does not involve free radicals but which involves the redistribution of the bonds in an intramolecular or intermolecular reactive complex without the liberation of radicals (see for example, Refs. 3–5). It is obvious that the choice between these two possibilities is extremely important for an understanding of the mechanism. It is not always a simple matter to make this choice, however, since the two reaction paths may lead to the same products, and direct methods for detecting radicals are usually insufficiently sensitive, particularly in the most important case of highly reactive radicals. These difficulties have been responsible for a number of errors and contradictions in published data on the mechanism of homolytic reactions in solution and emphasise the importance of the discovery of reliable criteria for distinguishing a free-radical mechanism.

In this review, the results of studies carried out by means of deuterium and mass spectrometry are examined critically and compared with data obtained by other methods.

II. THERMAL DECOMPOSITION OF BENZOYL PEROXIDE AND THE PHOTOLYSIS OF IODOBENZENE. PROPERTIES OF PHENYL RADICALS

The first paper in this field, published by Eliel and coworkers[6], described the thermal decomposition of acyl peroxides. It was found in particular that benzoyl and acetyl peroxides in a solution of benzene C_6H_5D give, among other products, biphenyl and toluene containing the d_2 isotopic forms. This observation provided further confirmation of the processes, established a short time earlier[7], involving the disproportionation of radicals formed by the attachment of phenyl radicals to benzene,

and also proved the analogous reactions with methyl radicals [see scheme (1)]†:



(1)

The origin of the products of the reaction of R· radicals with benzene is now explained on the basis of the disproportionation and also the dehydrogenation and dimerisation of radicals of type (A). It was suggested [6] that the first two of these reactions take place with a kinetic isotopic effect, determining the isotopic effect for the formation of diaryls or alkylaryls (the differences between their isotopic composition and the composition calculated from the original benzene). The existence of this last effect, the presence of the isotopic forms d_2 in the diaryls or alkylaryls obtained in benzene-d_1, and the formation of dihydrodiaryls or dihydroalkylaryls (C) in an inert atmosphere were regarded by Eliel and coworkers [8] as indications that free radicals R· take part in the reactions. We shall return to these indications later, but meantime we would point out that the authors cited were unable to explain the isotopic composition of the biphenyl obtained in experiments with benzoyl peroxide. This was done later (see below).

In subsequent work [9-12], the decomposition of benzoyl peroxide and the photolysis of iodobenzene were studied in benzene C_6D_6 (also containing the d_5, d_4, and d_3 forms), in benzene (C_6D_6 + C_6H_6), or in cyclohexane (C_6D_{12} + C_6H_{12}). The solvents after the experiments, the biphenyls obtained, and the unreacted iodobenzene were subjected to mass-spectrometric analysis.

It was found that the benzenes C_6H_5D and C_6H_6 are formed in the reactions; the ratio of the other forms of benzene remains unchanged; the cyclohexane is enriched in deuterium, but new isotopic forms are not produced; the iodobenzene does not contain the form C_6D_5I and other deuterated forms; the isotopic composition of the biphenyls from the experiments in benzene exhibit characteristic features, which are discussed in detail below.

The thermal decomposition of benzoyl peroxide [6,7,13,14] and the photolysis of iodobenzene [15-18] undoubtedly take place with the intermediate formation of free phenyl radicals. The observations listed above make it possible to reach a number of conclusions regarding the properties of these radicals and the mechanism of the reactions being considered, and to formulate the indications of the participation of free phenyl radicals in homolytic reactions.

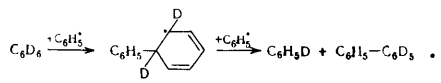
It has often been suggested (see for example Refs. 15, 16, 19-21), that phenyl radicals are capable of removing deuterium from heavy benzene:

$$C_6H_5^{\cdot} + C_6D_6 \rightarrow C_6H_5D + C_6D_5^{\cdot} \quad . \qquad (2)$$

Considerable importance was attributed to this process of "chain transfer" since it was assumed that it increases the "lifetime" of the phenyl radicals and the possibility of their reaction. A consequence of reaction (2) would be the formation of products containing C_6D_5 residues, namely C_6D_5I, $C_6D_5-C_6D_5$, $C_6D_5-C_6D_4H$, etc., formed by the recombination of $C_6D_5^{\cdot}$ with atomic iodine or by attachment to benzene from the medium. The iodobenzene after the experiments did not contain deuterium (see above), however, and the biphenyls did not contain forms with more than five deuterium atoms, and all the deuterium was present in one of the rings. Another consequence of reaction (2) with different isotopic forms of benzene from the medium should have been a change in the ratio of the quantities of these forms (as a result of the kinetic isotopic effect). In actual fact, however, the ratio does not change.

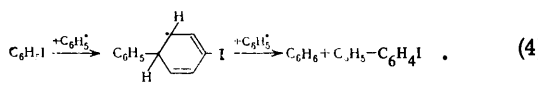
For these reasons it was concluded that "chain transfer" by the phenyl radicals does not take place to a significant extent either in its simplest form (2) or in a later version [20,22,23] involving a π complex of a radical and benzene. An analogous conclusion was reached on the basis of less direct data [24,25].

The formation of benzenes d_1 and d_0 in these experiments was attributed to reactions of type (3) with different isotopic forms of benzene from the medium:



This suggestion agrees with all the observations, since reactions (3) cannot lead to the formation of C_6D_5I or $C_6D_5-C_6D_5$ and should not lead to a change in the ratio of the heavy forms of benzene, since we should not expect significant kinetic isotopic effects in processes involving attachment to different isotopic forms of benzene.

The formation of benzene-d_0, however, cannot be attributed entirely to reactions (3), since in experiments in which the original benzene contained 95% deuterium, this reaction, for all possible values of the kinetic isotopic effect of its second stage, should give more benzene-d_1 than benzene-d_0, whereas the opposite was observed. Thus the formation of benzene C_6H_6 was attributed not only to process (3) but also to an analogous reaction of type (4) or, in the experiments with benzoyl peroxide, to processes of the same kind involving, instead of C_6H_5I, the peroxide or other aromatic compounds not containing deuterium.



(4)

This treatment, in particular, attributed the increase in the ratio C_6H_5D/C_6H_6 with decrease in the concentration of C_6H_5I or peroxide in benzene to the fact that the decrease leads to a decrease in the extent to which reaction (4) takes place. We shall see below that reactions of type (4) must be assumed in order to explain the isotopic composition of the biphenyls formed. It should also be noted that in the photolysis of iodobenzene, iodobiphenyl is in fact obtained [18].

In a medium of cyclohexane, benzenes-d_1 and -d_0 are formed by reactions (5), taking place with a kinetic isotopic effect, which explains the enrichment of the cyclohexane in deuterium after the experiments:

$$C_6H_5^{\cdot} + C_6D_{12} \rightarrow C_6H_5 + C_6D_{11}^{\cdot}; \; C_6H_5^{\cdot} + C_6H_{12} \rightarrow C_6H_6 + C_6H_{11}^{\cdot} \quad . \qquad (5)$$

The magnitude of this effect was found to be 9. It was measured [26] relative to the quantities of C_6H_5D and C_6H_6 formed in the photolysis of C_6H_5I, since it was shown that in a medium of cyclohexane, reaction (5) is the only source of benzenes-d_1 and -d_0.

The behaviour of phenyl radicals in toluene $C_6H_5CD_3$ has not been studied by this method. It will be shown in the next section, however, that a number of radicals which are less reactive than $C_6H_5^{\cdot}$ remove hydrogen from the methyl

†Here and subsequently, one of the possible formulae for cyclohexadienyl radicals is given.

group of toluene. It may therefore be assumed that hydrogen is also removed by phenyl radicals, and that published data [27] which deny this removal are in this respect erroneous.

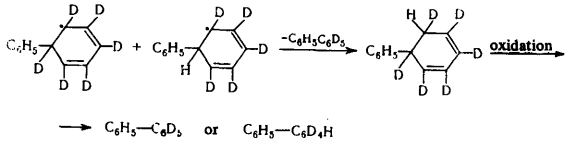
The reaction of the cyclohexyl radicals formed by reaction (5) was not specially studied in the works cited. From this work it followed, however, that C_6H_{11} radicals are not significantly capable of undergoing disproportionation and chain transfer:

$$C_6H_{11}^{\cdot} + C_6D_{11}^{\cdot} \rightarrow C_6H_{11}D + C_6D_{10}$$

$$C_6H_{11}^{\cdot} + C_6D_{12} \rightarrow C_6H_{11}D + C_6D_{11}^{\cdot} \qquad (6)$$

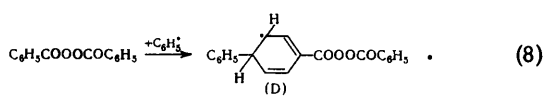
since the cyclohexane after the experiments did not contain the form $C_6H_{11}D$. This conclusion was later confirmed (see section III).

The isotopic composition of the biphenyls from these experiments shows that these substances are formed not only by the previously accepted schemes of types (3) and (7) involving various isotopic forms of benzene, but also by other paths. This followed from the results of a calculation which showed that the isotopic composition of the biphenyls obtained by schemes (3) and (7) or their combination differs from that observed experimentally: in the biphenyls the proportion of the d_0, d_1, and d_2 forms is higher, and among the other forms the proportion of d_5 is lower than that given by calculation. Allowance for kinetic isotopic effects does not give agreement between the calculated and experimental results.



(7)

The experimental results can be explained, however, if it is assumed that in addition to reactions (3) and (7), the photolysis of C_6H_5I involves the disproportionation of iodohydrobiphenyl radicals, formed according to scheme (4), with isotopic forms of hydrobiphenyl radicals, formed by reaction (3). Calculation shows that this process leads to a decrease in the proportion of the biphenyl-d_5 in the biphenyls-d_3, -d_4, and -d_5. Moreover, it leads to the formation of the iodobiphenyl-d_1. The latter, and also the iodobiphenyl-d_0, give on photolysis the radicals $C_6H_5C_6H_3D^{\cdot}$ and $C_6H_5C_6H_4^{\cdot}$, which, like phenyl radicals, remove hydrogen and deuterium from the medium, giving the biphenyls-d_0, -d_1, and -d_2. In the experiments with benzoyl peroxide, the isotopic composition of biphenyl is explained analogously: in addition to reactions (3) and (7), the process involves attack by the phenyl radicals on the peroxide (and other aromatic compounds present), for example:



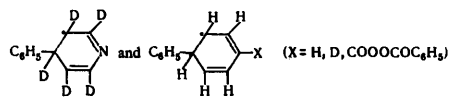
(8)

The radicals (D) after dehydrogenation and disproportionation give phenyl-substituted benzoyl peroxides-d_0 and -d_1, decomposition of which leads to the formation of $C_6H_5C_6H_4^{\cdot}$ and $C_6H_5C_6H_3D^{\cdot}$ radicals, which remove hydrogen and deuterium from the medium with the formation of the biphenyls-d_0, -d_1, and -d_2.

It will be shown below that the isotopic composition of the products of many reactions involving $C_6H_5^{\cdot}$ radicals in benzene are explained analogously.

Thus the isotopic composition of biphenyl results from the reactions of free radicals of various types. In biphenyl there is an increase in the concentration of the d_0, d_1, and d_2 forms, and a decrease in the concentration of the d_5 form. There characteristic features of the isotopic composition, as shown by Gragerov and coworkers (see for example, Refs. 10, 11, 27, 38, 74, 112), can be used to distinguish reactions involving $C_6H_5^{\cdot}$ free radicals in benzene from reactions taking place in the reactive complex. Another indication, as is clear from above, is the appearance of the benzenes-d_1 and -d_0 in benzene and cyclohexane after the experiments. It will be shown below that reactions which do not involve free radicals do not lead to the formation of the benzene-d_1 and -d_0 and give biphenyl with composition corresponding to that of the benzene solvent.

The thermal decomposition of benzoyl peroxide in heavy pyridine was studied recently [28] and it was shown that there is an extensive analogy in the reaction mechanisms in pyridine and in benzene. As in a medium of C_6D_6, the reaction gave the benzenes-d_1 and -d_0 and the products of the reaction of the C_6H_5 residues with the solvent—phenylpyridines, and also biphenyl. These results were attributed to the free-radical mechanism of the process. It was confirmed by the isotopic composition of the phenylpyridine and biphenyl, which could be explained only by assuming reactions, similar to those examined above, undergone by radicals of type (9), formed by the attachment of C_6H_5 to the isotopic forms of pyridine and the aromatic compounds present in the system



(9)

The experiments showed that the benzenes-d_1 and -d_0 are not formed by direct removal of hydrogen from pyridine:

$$C_6H_5^{\cdot} + NC_5D_5 \rightarrow C_6H_5D + NC_5D_4^{\cdot} \qquad (10)$$

since the reaction was not accompanied by a change in the ratio of the quantities of its isotopic forms and did not give heavy bipyridyls (the probable products of the attachment of pyridyl radicals to pyridine). The formation of the benzenes-d_1 and -d_0 was attributed to the dehydrogenation of radicals (9) by phenyl radicals.

III. PHOTOLYSIS OF ORGANIC HALIDES AND THE PROPERTIES OF THE CORRESPONDING RADICALS

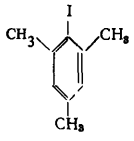
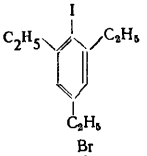
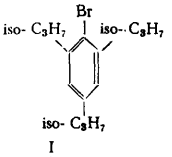
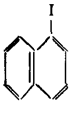
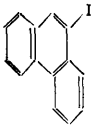
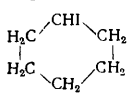
The free-radical mechanism of the photolysis of organic halides is firmly established [11,16,18,29,30], and this reaction provides a convenient and general source of free radicals. It is used in studies carried out by means of deuterium and mass spectrometry to investigate the properties and the mechanism of the reactions of hydrocarbon radicals. Simple aliphatic, substituted phenyl, aryl, and arylalkyl radicals and various radicals stabilised by conjugation have been studied in various solvents. A summary of the reactions studied and references to the corresponding literature are given in the Table.

The chief result of these studies is the establishment of the extensive similarity between a number of radicals and phenyl radicals and the discovery of the general regular features of their behaviour and of criteria which make it possible to detect the participation of free hydrocarbon radicals in reactions whose mechanism has not been established. Specific properties have been found only for the

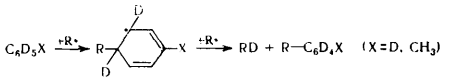
benzyl and cyclohexyl radicals, which will be examined separately.

The R' radicals studied (with the exception of the benzyl and cyclohexyl radicals), in the reactions given in the Table, give the hydrocarbons RD and RH. As with the phenyl radicals, the isotopic composition of the benzene, toluene with deuterium in the ring, and naphthalene after the experiments remains the same as that for the original solvents, whereas cyclohexane and toluene with deuterium in the methyl group are usually enriched in deuterium. The products of the direct removal of hydrogen from benzene by R' radicals are not obtained.

Reactions involving the photolysis of organic halides (the symbol + denotes that the reaction has been studied).

Halides	Heavy solvents: benzene	cyclohexane	deuteromethyltoluene	toluene with deuterium in the ring	naphthalene	triphenyldeuteromethane	References
p-$C_6H_5C_6H_4I$	+	+	+	−	−	−	31–33
	+	+	+	+	−	−	34
	+	+	+	+	−	−	34
	+	+	+	−	−	−	34
	+	+	+	+	+	−	31–33
	+	−	−	−	−	−	35
$C_6H_5CH_2I$	+	+	+	+	−	+	32,33,36
$(C_6H_5)_2CHBr$	+	−	−	−	−	−	35
$CH_2{=}CH{-}CH_2I$	+	+	+	−	−	−	35
	+	+	+	−	+	+	32,33,36
CH_3I	+	+	−	−	−	−	12,37–39
C_2H_5I	+	+	−	−	−	−	12,37–39

These facts were interpreted by assuming that the radicals R', like phenyl radicals, remove hydrogen directly from cyclohexane and the methyl group of toluene, but not from benzene, the toluene ring, or naphthalene. They add on to the latter and remove hydrogen from the resulting radicals of the cyclohexadienyl type, according to a scheme analogous to (3), for example:



(11)

This course of the reactions is confirmed by the fact that in a number of instances, products of the type RC_6D_4X have been isolated or their formation established from the mass spectra. Their isotopic composition, like the composition of the biphenyl formed by the reaction of phenyl radicals with benzene (section II), usually differed from that calculated entirely according to a scheme of type (11): the products contained less than the calculated quantity of the d_4 form and more than the calculated quantities of the d_0 and d_1 forms [12,34,37–39]. These characteristic features of the isotopic composition were explained by assuming that the formation of these substances, in addition to reactions of type (11), also involves processes of type (1b) including a disproportionation stage.

The hydrocarbons (RH + RD) obtained in these reactions contain much more of the d_0 than d_1 form even in experiments with highly deuterated solvents. As with the phenyl radicals, this was explained by assuming that the hydrocarbons RH are obtained not only by the above reactions with heavy solvents, which give the compounds RD and RH, but also by the reaction of the R' radicals with the original aromatic halides and other light aromatic compounds [according to a scheme analogous to (4)] or by the direct removal of hydrogen from aliphatic halides, other aliphatic compounds present in the system, and aliphatic substituents in the aromatic rings.

These data made it possible to formulate criteria for the participation of R' free radicals in reactions whose mechanisms have not been established. These are: 1) the appearance of the hydrocarbons RD and RH in reactions in a medium of heavy benzene, cyclohexane, toluenes with deuterium in the ring or in the methyl group, and naphthalene; 2) the presence in the products of the type $R{-}C_6H_5$, obtained in heavy benzene, of larger quantities of the isotopic d_0 and d_1 forms and smaller quantities of the d_5 form than expected by calculation according to a scheme of type (11).

Benzyl radicals in aromatic media behave like the other radicals examined above. Unlike the latter, however, they do not remove hydrogen at 30–40° from the methyl group of toluene or from cyclohexane (but they remove it from the C–H group of triphenylmethane). Thus not all of the critieria for a free-radical mechanism, formulated above, apply to benzyl radicals.

It was found that cyclohexyl radicals cannot remove hydrogen at 30–40°C from benzene, toluene, cyclohexane, naphthalene, or the CH groups of triphenylmethane, either directly or through intermediate attachment to aromatic rings. Thus the method examined here cannot be used to indicate these radicals.

It should be noted, however, that the properties of cyclohexyl radicals raise a number of problems. For example, the reason for their low reactivity compared with benzyl radicals, and the mechanism of formation of light cyclohexane and cyclohexene obtained by photolysis of iodocyclohexane in heavy media [33,36], are not understood. This makes it uncertain whether the photolysis of $C_6H_{11}I$ does in fact give free radicals C_6H_{11}, particularly in view of the recent report [40,41] that the cyclohexyl radicals obtained by the photolysis and thermal decomposition of $Pb(C_6H_{11})_4$ and $Pb_2(C_6H_{11})_6$ in benzene remove hydrogen from the medium. It should be remembered, however,

that the $C_6H_{11}^{\cdot}$ radicals formed by the removal of hydrogen from cyclohexane under the influence of phenyl radicals do not disproportionate and do not remove hydrogen from cyclohexane [12]. The same was found for the $C_6H_{11}^{\cdot}$ radicals produced by the action of naphthyl radicals on cyclohexane [31-33]. Thus the properties of cyclohexyl radicals require further study.

Some other remarks and comparisons may be made regarding these data.

The study of 2,4,6-trialkylphenyl radicals was of interest in connection with the fact that steric hindrance can alter the properties of radicals considerably. The data show, however, that the properties of these radicals are qualitatively analogous to the properties of $C_6H_5^{\cdot}$ radicals.

Allyl radicals, as expected (but contrary to certain published work [42]), are much more reactive than benzyl radicals. It is difficult to reconcile their ability to remove hydrogen from cyclohexane with the data in Ref. 43 and with some of the data in Ref. 42.

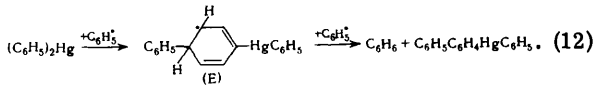
The reaction of diphenylmethyl radicals with benzene contradicts the data of Ref. 44, which are apparently erroneous in this respect. It must be assumed that these radicals, like benzyl radicals, do not react at low temperatures with cyclohexane and the methyl group of toluene.

IV. VARIOUS REACTIONS OF ORGANOMETALLIC COMPOUNDS

The mechanism of the photolysis of diphenylmercury was not elucidated completely by a large number of studies, carried out in particular by the isotopic method. Thus in Refs. 15, 19, 21, 22 it was concluded that this reaction in benzene takes place by a free-radical mechanism, whereas in Refs. 45 and 46 it was concluded that the reaction takes place in the reactive complex, without the liberation of radicals. The photolysis in cyclohexane and cyclohexene was explained by means of a free-radical scheme [46,47].

The use of a combination of the isotopic and mass-spectrometric methods showed [12,37-39] that the photolysis in benzene or in cyclohexane takes place by a free-radical mechanism, and also made it possible to determine various details of the mechanism.

In heavy solvents it was established that the benzenes-d_1 and -d_0 are formed, and this provided proof that $C_6H_5^{\cdot}$ radicals take part in the reaction. The fact that the form C_6H_6 predominates in the experiments in benzene was attributed, as with the photolysis of iodobenzene and the decomposition of benzoyl peroxide, to the fact that this form, unlike C_6H_5D, is obtained not only by a reaction of type (3) with the forms of benzene from the medium, but also by a reaction analogous to (4), involving diphenylmercury:



(12)

Further proof of the free-radical mechanism of the photolysis of diphenylmercury in benzene is provided by the characteristic features of the isotopic composition of the biphenyl produced. This does not contain biphenyls with more than five deuterium atoms and contains more of the d_0, d_1, and d_2 forms, and less of the d_5 form, than required by calculation according to reactions (3), (7), or their combinations, with any possible kinetic isotopic effects. This observation was attributed to the fact that the disproportionation of type (7) involves the radicals (E), which do not contain deuterium, and this leads to a decrease in the concentration of the d_5 form in the biphenyl obtained and to the appearance of $C_6H_5C_6H_4HgC_6H_5$ and $C_6H_5C_6H_3DHgC_6H_5$ molecules, which on photolysis give $C_6H_5C_6H_4^{\cdot}$ and $C_6H_5C_6H_3^{\cdot}$ radicals; the latter remove hydrogen and deuterium from the medium, with the formation of the biphenyls-d_0, -d_1, and -d_2.

The isotopic composition of the undecomposed biphenylmercury residue was also studied, and it was found that it does not contain deuterium. These results are of interest in connection with the fact that the introduction of tracer from the benzene into the diphenylmercury during photolysis was considered [15,21,22] to be one of the most important proofs of the existence of "chain transfer" of phenyl radicals (see section II). The introduction was not confirmed in subsequent work by the same authors [45,46].

Recently, they returned again [41,48] to the study of the photolysis and thermal decomposition of diphenylmercury, and also the photolysis and thermal decomposition of tetraphenyl-lead and hexaphenyldilead in heavy benzene, this time using the isotopic and mass-spectrometric methods. It was established that the reactions give the benzenes-d_1 and -d_0 and biphenyls of three kinds: unlabelled—A, labelled in one ring—B, and labelled in two rings—C. The mechanism of these reactions was examined for the example of the photolysis of diphenylmercury. The biphenyl A, in the opinion of the authors cited, is obtained as a result of the intramolecular decomposition, catalysed by mercury, of part of the diphenylmercury, with recombination of the radicals on the metal surface. We have seen, however, that another explanation for the appearance of this biphenyl is possible.

The formation of the biphenyl B was attributed to two mechanisms—decomposition in the reactive complex and free-radical reaction according to schemes (3) and (7)—and the production of the biphenyl C was attributed to free-radical "chain transfer" (2) and attachment of the radicals $C_6D_5^{\cdot}$, $C_6D_4H^{\cdot}$, etc., formed according to scheme 2, to the isotopic forms making up the heavy benzene.

It was later shown [49] that the biphenyls A, B, and C are also obtained in the photolysis and thermal decomposition of triphenylbismuth in heavy benzene, and the same explanations were put forward.

The formation of the biphenyl C in photolysis at low temperatures and the conclusion, on this basis, that "chain transfer" of phenyl radicals takes place do not agree with the work on the photolysis of diphenylmercury [11,37-39] or with other data on the behaviour of phenyl radicals in heavy benzene (see section II). The following considerations also cast doubt on the correctness of this observation. The isotopic composition of the biphenyl C can readily be calculated from the composition of the benzene solvent. The results of the calculation, however, show a marked lack of correspondence with the composition found in the works cited. It may therefore be assumed that that part of the work which refers to the production of the biphenyl C and the "chain transfer" in the photolysis is erroneous. It is not excluded, however, that "chain transfer" is observed at high temperatures, under the conditions of the thermal decomposition.

The decomposition and oxidation of diphenylzinc in heavy benzene have been studied [50,51]. Both reactions led to the appearance of the benzenes-d_1 and -d_0 and gave the biphenyls A and B, together with a small quantity of C in the thermal decomposition. The formation of the biphenyl A was attributed to intramolecular decomposition or oxidation of $Zn(C_6H_5)_2$, and the formation of the biphenyl B was attributed to reaction between the solvent and $C_6H_5^{\cdot}$ radicals

formed on decomposition or oxidation. Under the conditions of the thermal decomposition, the diphenylzinc underwent isotopic exchange with benzene. It must therefore be assumed that the biphenyl C was obtained by reaction between the solvent and labelled phenyl radicals from the organometallic compound, which had undergone partial exchange.

It was recently established [28] that the photolysis of diphenylmercury in heavy pyridine takes place by a free-radical mechanism. All that has been said regarding the decomposition of benzoyl peroxide in pyridine (section II) applies to the mechanism of this reaction.

V. REACTIONS OF DIAZO- AND AZO-COMPOUNDS

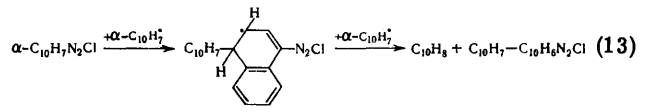
Despite extensive published material [3,14,30,52-55], the participation of free radicals in the thermal decomposition of diazonium salts was disputed—evidence was published for [30,56,57] and against [58] this suggestion. The same is true of the thermal decomposition of nitrosoacetanilide (NAA) [14,30,53,55] and phenylazotriphenylmethane (PAT) [59]: evidence has been put forward for [60-70] and against [8,22,58] a free-radical mechanism. Confirmation was also required for the free-radical mechanism of the Gomberg–Bachmann reaction [14,30,52,53,55,71,72]. The mechanism of the arylation of benzene by aromatic amines under the influence of isopentyl nitrite in neutral medium [73] was not studied. Studies of these reactions by a combination of the isotopic and mass-spectrometric methods are discussed below.

The decomposition of phenyldiazonium fluoroborate and chloride was studied in various deuterated solvents [9,10,12,38,39,74,75]. In benzene, cyclohexane, toluene $C_6D_5CH_3$, bromobenzene, and chloroform, the fluoroborate did not give the benzenes-d_1 and -d_0, and the biphenyl obtained in a medium of benzene had an isotopic composition corresponding to the combination of the C_6H_5 residues from the salt and from the solvent. Thus $C_6H_5^{\cdot}$ radicals do not take part in the decomposition of $C_6H_5N_2BF_4$. $C_6H_5^{+}$ ions (whose reactions were detected in some examples of the decomposition of the fluoroborate [76,77]) apparently do not take part in the decomposition either, since it may be assumed that these ions, like Alk^+ ions, which remove hydrogen from Alk–H molecules [78,79], react with the solvents to give the benzenes-d_1 and -d_0. The decomposition of $C_6H_5N_2BF_4$ takes place in the reactive complex.

The decomposition of $C_6H_5N_2Cl$ in the same solvents, on the other hand, gave the benzenes-d_1 and -d_0, and the biphenyl obtained in a medium of benzene had the isotopic composition characteristic of free-radical reactions. Thus $C_6H_5^{\cdot}$ free radicals take part in this reaction. Their yield, however, is much less than that in the other reactions examined, since the yield of benzenes-(d_1 + d_0) is unusually small. The process probably takes place in two directions—by the free-radical mechanism and in the reactive complex—with the latter direction predominating.

In the decomposition of $C_6H_5N_2BF_4$ in heavy pyridine and α- and β-picolines with deuterium in the methyl group, all the indications of the participation of $C_6H_5^{\cdot}$ free radicals were observed (the formation of the benzenes-d_1 and -d_0, and the characteristic isotopic composition of the phenylpyridine), whereas in the decomposition of $C_6H_5N_2Cl$ they were observed only in a medium of picolines. The fluorobenzene and chlorobenzene formed in these reactions did not contain deuterium.

The intermediate formation of free radicals was established in the thermal decomposition of α-naphthyldiazonium chloride [32,33,80] in heavy benzene, cyclohexane, and naphthalene. The reaction led to the formation of the naphthalenes-d_1 and -d_0, obtained by direct removal of hydrogen from cyclohexane and according to schemes of types (11) and (13):



$$\alpha\text{-}C_{10}H_7N_2Cl \xrightarrow{+\alpha\text{-}C_{10}H_7^{\cdot}} C_{10}H_7\text{-}N_2Cl \xrightarrow{+\alpha\text{-}C_{10}H_7^{\cdot}} C_{10}H_8 + C_{10}H_7\text{–}C_{10}H_6N_2Cl \quad (13)$$

The last reaction is analogous to scheme (4).

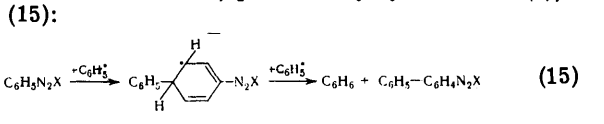
The chloronaphthalene from these experiments did not contain deuterium, so that it was not formed by chlorination of the naphthalene by atomic chlorine. The chloronaphthalene was possibly obtained in the "solvent cage":

$$\alpha\text{-}C_{10}H_7N_2Cl \xrightarrow{-N_2} (\alpha\text{-}C_{10}H_7^{\cdot} + Cl^{\cdot}) \rightarrow \alpha\text{-}C_{10}H_7Cl \quad (14)$$

and the low yields may be due to the fact that most of the radicals leave the "cage" and do not give this substance. It is not excluded that some chloronaphthalene is obtained by a reaction which does not involve free radicals, as with the halogenobenzenes.

To explain these results, it was suggested [75] that the free-radical mechanism of decomposition of diazonium salts plays a greater role, the more stable the radicals formed, and that this stability is determined not only by their chemical character but also by solvation. It was still not clear, however, why the decomposition of $C_6H_5N_2Cl$ in pyridine takes place by a reaction which does not involve free radicals.

The decomposition of NAA and PAT in heavy benzene or cyclohexane [81] takes place by a free-radical mechanism. It gave benzenes-d_1 and -d_0, presumably by reactions (3), (5), and (15):



$$C_6H_5N_2X \xrightarrow{+C_6H_5^{\cdot}} C_6H_5\text{-}N_2X \xrightarrow{+C_6H_5^{\cdot}} C_6H_6 + C_6H_5\text{–}C_6H_4N_2X \quad (15)$$

X = –OCOCH$_3$ or –C(C$_6$H$_5$)$_3$

to which, in the case of PAT, was added reaction with the triphenylmethanes formed in the experiments:

$$C_6H_5^{\cdot} + (C_6H_5)_3CH \text{ (or } (C_6H_5)_3CD) \rightarrow C_6H_6 \text{ (or } C_6H_5D) + (C_6H_5)_3C^{\cdot} \quad (16)$$

The latter were evidently obtained by the removal of hydrogen or deuterium from radicals of the cyclohexadienyl type by $(C_6H_5)_3C^{\cdot}$ radicals according to schemes of types (3) and (15) with $(C_6H_5)_3C^{\cdot}$ instead of $C_6H_5^{\cdot}$ in the second stages. The formation of triphenylmethanes confirmed indirectly the free-radical mechanism of the decomposition of PAT. Direct confirmation was obtained by the EPR method, which made it possible to identify the triphenylmethyl radicals.

Eliel and coworkers [8] found, however, that in the decomposition of NAA and PAT in benzene-d_1, biphenyl is obtained without a kinetic isotopic effect and does not contain the d_2 form, and the products of the reactions in an inert atmosphere do not contain dihydrobiphenyl. This absence of the "indications of the participation of free radicals in the reactions" (see section II) was interpreted as proof that the decomposition of NAA and PAT takes place by a mechanism which does not involve free radicals.

We cannot agree with this intrepretation. It has been correctly noted [64] that all the above "indications" of Eliel and coworkers are the result of disproportionation of radicals of the cyclohexadienyl type (see section II). Their presence proves that the reactions take place by a free-radical mechanism, but their absence merely indicates that disproportionation does not take place.

It has also been demonstrated[81] that disproportionation does not take place, since the biphenyls obtained in the work cited contained the forms from d_5 to d_2 in the ratio corresponding to that calculated according to scheme (3).

Disproportionation of radicals of the cyclohexadienyl type is apparently suppressed by more rapid reactions involving dehydrogenation and combination with $(C_6H_5)_3C^\cdot$ or $C_6H_5-N=N-O^\cdot$ radicals, which are formed in appreciable concentrations, because of their relative stability[64,68].

The biphenyls in the experiments being discussed[81] contained larger quantities of d_1 and d_0 forms relative to those calculated according to scheme (3), and a source of these forms, in addition to reactions (3), is provided by the thermal decomposition of $C_6H_5C_6H_4N_2X$ molecules formed according to scheme (15), and the removal of hydrogen and deuterium from the medium by the $C_6H_5C_6H_4^\cdot$ radicals produced (see section II). Thus the isotopic composition of the biphenyls also indicates that the thermal decomposition of NAA and PAT takes place by a free-radical mechanism.

Of the Gomberg–Bachmann reactions, the reactions of $C_6H_5N_2Cl$, α-$C_{10}H_7N_2Cl$, and p-$C_6H_5C_6H_4N_2Cl$ with aqueous alkali in benzene and cyclohexane have been studied[10,12,38,39,74] and the free-radical mechanism of these reactions has been proved. Like other free-radical processes, the reactions led to the formation of the benzenes-d_1 and -d_0, the naphthalenes-d_1 and -d_0, and the biphenyls-d_1 and -d_0 respectively, obtained by the direct removal of hydrogen from cyclohexane by the radicals according to schemes of types (3) and (11) and by reactions analogous to reactions (13) and (15). The biphenyl from the experiments with $C_6H_5N_2Cl$ in benzene contained smaller quantities of the d_5 form and larger quantities of the d_0, d_1, and d_2 forms relative to those calculated according to scheme (3), and this again indicated that the reaction takes place by a free-radical mechanism. In the experiment with $C_6H_5C_6H_4N_2Cl$, in accordance with the free-radical scheme, one of the products was terphenyl.

The reaction of aromatic amines $ArNH_2$ with isopentyl nitrite was studied in heavy benzene, cyclohexane, or naphthalene[82] with the compounds aniline, p-nitroaniline, p-anisidine, α-, and β-naphthylamines, p-aminobiphenyl, and γ-aminopyridine. A free-radical mechanism was found for all these reactions: the products contained the compounds ArD and ArH, formed, as usual, by the removal of hydrogen from cyclohexane by Ar$^\cdot$ radicals according to reactions of type (11) with benzene or naphthalene and also ArH formed by the removal of hydrogem from isopentyl nitrite and its reaction products by the radicals, and also by a reaction analogous to reaction (11), but with the original amines instead of benzene or naphthalene. The last reaction, in the case of aniline, should give aminobiphenyl, which, by reacting with isopentyl nitrite, leads to the formation of the biphenyls-d_1 and -d_0. These were in fact found in the experiment with aniline in benzene in quantities greater than that calculated according to scheme (11). In the other experiments the isotopic composition of the products of the arylation of benzene coincided with that calculated according to this scheme. Thus in this instance, as in the decomposition of NAA and PAT, the disproportionation of radicals of the cyclohexadienyl type is not significant. This reaction is apparently suppressed by the more rapid dehydrogenation, possibly under the influence of isopentyl nitrite or its decomposition products.

The radicals β-$C_{10}H_7^\cdot$, p-$O_2NC_6H_4^\cdot$, p-$CH_3OC_6H_4^\cdot$, and γ-$NC_5H_4^\cdot$, obtained by the reaction of the corresponding amines with isopentyl nitrite, were first studied in the work cited by means of a combination of isotopic and mass-spectrometric methods. From the foregoing it follows that their behaviour in benzene, cyclohexane, and naphthalene does not differ from that of other aryl or simple alkyl radicals.

In the work cited it was suggested that diazo-hydroxides are formed in intermediate stages:

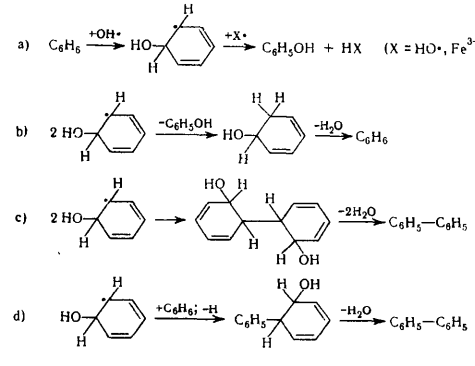
$$ArNH_2 + C_6H_{11}ONO \xrightarrow{-C_6H_{11}OH} ArNHNO \rightarrow Ar-N=N-OH \quad . \qquad (17)$$

The same substances are obtained in the first stages of the Gomberg–Bachmann reaction. The similarity in the mechanisms of the two reactions was recently confirmed[83] by the fact that in the reaction of aniline with isopentyl nitrite in benzene the EPR method established the existence of the same radicals $C_6H_5-N=N-O$, which were recently assumed[72] to be intermediate products of the Gomberg–Bachmann reaction.

VI. PROCESSES OF HYDROCARBON OXIDATION

It has been shown by isotopic and mass-spectrometric methods[12,38,84,85] that in the oxidation of a mixture of benzenes C_6D_6 and C_6H_6 by potassium permanganate in acid medium or by ammonium peroxosulphate catalysed by Ag^+ ions, the unreacted hydrocarbon residue does not contain the benzene-d_1. It was assumed that radicals are formed in the intermediate stages of the oxidation of organic compounds by permanganate (for example Refs. 86 and 87) and by peroxosulphate (for example Ref. 88). The results given above show that in the examples being considered these radicals cannot be $C_6H_5^\cdot$ radicals. On the other hand, the radiolysis of dry benzene ($C_6D_6 + C_6H_6$) gave biphenyl with the isotopic composition corresponding to a free-radical scheme of formation, confirming the previously assumed (for example Ref. 89) participation of $C_6H_5^\cdot$ radicals in this reaction.

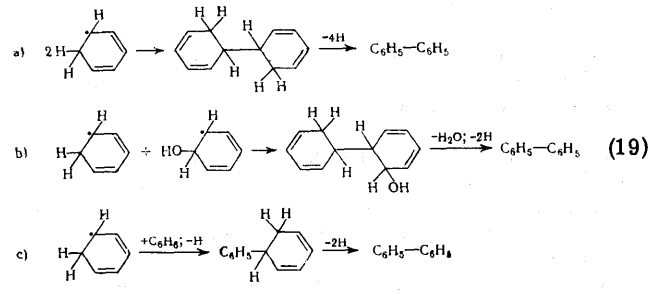
$C_6H_5^\cdot$ radicals are not obtained in the oxidation of heavy benzene by Fenton's reagent or pernitrous acid or in the radiolysis of a degassed water–benzene mixture[12,84,85,90]. These data refuted the commonly encountered schemes for radiolysis and oxidation by Fenton's reagent involving the participation of phenyl radicals (for example Refs. 91–94), assumed to be produced by the removal of hydrogen from benzene by OH$^\cdot$ radicals. We give below alternative schemes (for example Refs. 93–96) in which OH$^\cdot$, like other radicals, do not remove hydrogen from benzene, but add on to it:



(18)

The isotopic composition of the products of these reactions made it possible to refine these schemes and to obtain new data on the mechanism.

The composition of the biphenyls concided with that calculated for reactions (18*c*) or (18*d*). For the radiolysis, it made it possible to reject another possible mechanism—the formation of biphenyl from $C_6H_7^{\cdot}$ ($C_6D_7^{\cdot}$) radicals, assumed to be formed [97,98] by the attachment of hydrogen atoms from the water to benzene:

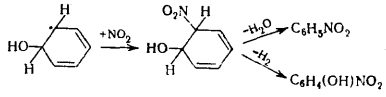


(19)

since the isotopic composition of the biphenyl differed sharply from that calculated according to schemes (19). Disproportionation of the radicals $C_6H_7^{\cdot}$ and $C_6D_7^{\cdot}$ does not take place either. This would have given (after dehydrogenation of the C_6H_7D disproportionation product) the benzene-d_1, which was not detected.

The phenol obtained in oxidation with Fenton's reagent had an isotopic composition close to that calculated according to scheme (18*a*) but markedly different from that corresponding to scheme (18*b*) with allowance for the dehydrogenation of dihydrophenol. Thus disproportionation of the hydrophenol radicals (18*b*), if it takes place at all, does not take place to a significant extent. This is apparently related to the high concentration of oxidising agents (Fe^{3+}, H_2O_2) in the reaction system; these rapidly dehydrogenate the radicals according to reaction (18*a*). The results obtained confirm schemes (18*a*), (18*c*), and (18*d*).

It has been suggested [99] that in the reaction of benzene with pernitrous acid, nitrobenzene and nitrophenol are formed according to the scheme:

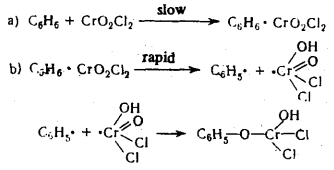


(20)

The isotopic composition of the reaction products showed that the removal of water and hydrogen takes place with a kinetic isotopic effect and therefore takes place in the slow stages of reactions (20). Another possible mechanism for the formation of nitrophenol—hydroxylation of nitrobenzene—cannot be distinguished from mechanism (20) on the basis of the results being discussed. It should be noted that a mechanism which does not involve free radicals is also possible for oxidation by pernitrous acid [12] and that the results being discussed do not make it possible to choose between this and scheme (20).

In the mechanism of the oxidation of hydrocarbons by chromyl chloride (Etard's reaction), the problem of the nature of the first, most important, oxidative stage, which is complete with the formation of an insoluble complex of the hydrocarbon and CrO_2Cl_2, was unresolved. Ionic (for example Ref. 100), radical [101-103], and molecular [104] mechanisms were proposed for this stage. It was recently shown [103] that the free-radical scheme agrees with all published data, but direct confirmation was given only in Refs. 9, 10, 12, 32, 38, 105. In these experiments, mixtures of light and heavy benzene, toluene, and naphthalene or solutions of toluene, diphenylmethane, biphenyl, naphthalene, anthracene, and phenanthrene in heavy benzene or in heavy cyclohexane were subjected to incomplete oxidation. It was found that the unreacted residues of the oxidised hydrocarbons contained their d_1 isotopic forms, indicating the intermediate formation of the radicals corresponding to the hydrocarbons. The oxidation of toluene and diphenylmethane in benzene gave further proof of the intermediate formation of benzyl and diphenylmethyl radicals—the isolation of benzophenone and triphenylcarbinol, which are products of the oxidation of diphenylmethane and triphenylmethane, formed by the addition of the $C_6H_5CH_2^{\cdot}$ or $(C_6H_5)_2CH^{\cdot}$ radicals to benzene according to scheme (11).

In the works cited and in Ref. 106 it was established that a kinetic isotopic effect is not observed in the oxidation of benzene and naphthalene by CrO_2Cl_2, but that this effect is observed in the oxidation of toluene and triphenylmethane. The reaction scheme finally proposed is given below for the example of benzene:



(21)

(22)

Analogous reactions take place with the second molecule of the oxidising agent. Reaction (22) competes with the usual reactions of $C_6H_5^{\cdot}$ radicals in benzene—reaction (3), which gives benzene-d_1, and reaction (7). In some instances, for example in the oxidation of toluene and triphenylmethane, the slow stage is stage (21*b*), and this leads to a kinetic isotopic effect.

The participation of free radicals in Etard's reaction was recently confirmed directly by the EPR method [107].

VII. REACTIONS OF ORGANIC HALIDES WITH METALS

The participation of free radicals in the mechanism of the reactions of organic halides with metals is often assumed, but it has been demonstrated convincingly in only a few studies. Studies of the reactions of magnesium, lithium, sodium, potassium, and copper with organic halides by a combination of isotopic and mass-spectrometric methods are discussed below. These studies not only proved that these reactions involve free radicals, but also revealed many aspects of their mechanisms.

A number of authors (for example Refs. 108 and 109) assumed on the basis of indirect data that reactions of this kind involving magnesium take place by a free-radical mechanism. This was subsequently confirmed more convincingly [110,111], but it was still not clear whether this mechanism was general and whether it still holds in the presence of ether, in which preparative syntheses are usually carried out.

In the study of the reaction of magnesium with iodobenzene in heavy benzene or cyclohexane [9,10,12,38,39,112], the substances A isolated directly from the reaction mixture and the substances B obtained by the action of water on the residue from the complete separation of compounds A were analysed separately. Benzenes-d_0 and -d_1 were found in the compounds A, indicating that the free radicals $C_6H_5^{\cdot}$ take part in the reactions. The formation of the radicals was explained by the scheme:

$$C_6H_5I + Mg \rightarrow C_6H_5^{\cdot} + MgI^{\cdot} \rightarrow C_6H_5MgI \qquad (23)$$

and the formation of the benzenes-d_1 and -d_0 was explained by the usual schemes (3), (4), and (5). In the biphenyl A from the experiments in benzene, the proportions of the

forms from d_5 to d_2 corresponded to those calculated according to scheme (3), whereas the proportions of the d_1 and d_0 forms were found to be much greater. Thus reactions of type (3) provide the main source of the biphenyls from d_5 to d_2, and the disproportionation (7) is not significant. The formation of the biphenyl-d_0 was attributed to the reaction:

$$C_6H_5MgI + C_6H_5I \rightarrow C_6H_5{-}C_6H_5 + MgI_2 \quad (24)$$

and the formation of the biphenyls-d_1 and some -d_0, as in other examples of reactions involving phenyl radicals in benzene, was attributed to the removal of hydrogen or deuterium from the medium by $C_6H_5C_6H_4^{\cdot}$ radicals. The latter were produced from iodobiphenyl [formed by reaction (4)] by a scheme similar to schemes (23) or (26) (see below).

The benzene B was formed by the reaction

$$C_6H_5MgI + H_2O \rightarrow C_6H_6 + MgIOH \quad . \quad (25)$$

It did not contain deuterium, indicating the absence of isotopic exchange between C_6H_5MgI and benzene (discovered earlier [113]). The biphenyl B from the experiment in benzene was apparently obtained analogously from $C_6H_5C_6H_4MgI$. It contained a small quantity of deuterium, probably as a result of isotopic exchange between $C_6H_5C_6H_4MgI$ and biphenyl A under the severe conditions of the separation of the latter. The compounds B obtained in benzene or cyclohexane included hydrogen (H_2 + HD). The formation of HD molecules was attributed to the dehydrogenation of radicals of the hydrobiphenyl type by the species $MgI^{\cdot}$ or to the removal of hydrogen from cyclohexane by these species and reaction of the resulting MgID molecules with water. The existence of compounds of the type MgIH was recently confirmed [114]. The biphenyls A and B from the experiments in cyclohexane did not contain deuterium, since they were formed by reaction (24) and by the reaction of $C_6H_5C_6H_4MgI$ with water.

It may be noted that the possibility of formation of radicals by reactions of type (23) has been doubted (see for example Refs. 109 and 110) and it has been suggested that the radicals are obtained in processes described by overall equations of type (24). Special experiments [115] confirmed that reaction (24) takes place by a free-radical mechanism. This does not alter the essential features of the interpretation given for the mechanism of reaction of iodobenzene with magnesium, but only modifies stage (24), interpreting it as a radical reaction:

$$C_6H_5MgI + C_6H_5I \rightarrow MgI_2 + 2C_6H_5^{\cdot} \quad (26)$$

It must be assumed that most of the $C_6H_5^{\cdot}$ radicals formed according to this scheme combine in a "solvent cage", and this explains the high percentage of the d_0 form in the biphenyl obtained in benzene C_6D_6 according to reaction (26) and in the biphenyl A.

Returning to process (23) and the analogous reaction of $C_6H_5C_6H_4I$, we may note that their free-radical mechanism was assumed [12] because it was impossible to explain the formation of hydrogen HD without assuming the participation of $MgI^{\cdot}$ radicals. $MgI^{\cdot}$ radicals may also be obtained, however, by the thermal decomposition of organomagnesium compounds (see below and Ref. 116). Thus the free-radical nature of reaction (23) and its analogues has not yet been proved.

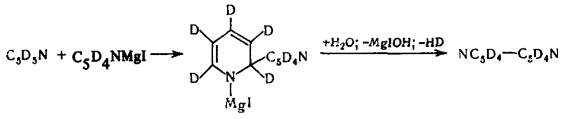
It has been shown [33, 115] that the free-radical mechanism of the reaction of magnesium with iodobenzene is preserved in the presence of ether. Free-radical mechanisms were also found for the reactions of magnesium with α-iodonaphthalene in heavy benzene, with p-iodobiphenyl in heavy benzene mixed with ether and in heavy cyclohexane mixed with ether, and with benzyl chloride in heavy benzene mixed with ether. These reactions gave naphthalenes-d_1 and -d_0, biphenyls-d_1 and -d_0, and toluenes-d_1 and -d_0 respectively. Moreover, terphenyl was obtained in the experiments with iodobiphenyl in benzene/ether, and diphenylmethane and bibenzyl were obtained in the experiments with benzyl chloride.

The mechanism of these reactions is analogous to that examined above: the hydrocarbons RD and RH were obtained according to schemes (11), (5), and (4) with light aromatic compounds and by removal of hydrogen from ether by the radicals. Terphenyl and diphenylmethane were formed according to schemes of type (11), and bibenzyl was formed by the combination of benzyl radicals. The radicals were apparently produced by reactions analogous to reactions (26) and possibly (23).

The reaction of iodobenzene with magnesium in heavy pyridine takes place in unique fashion [28]. At 60° the isotopic composition of its products and its mechanism are analogous to the composition of the products and the mechanism of the decomposition of benzoyl peroxide and the photolysis of diphenylmercury in pyridine (sections II and IV). At 120°, the ratio of the isotopic forms in the solvent changes, and phenylpyridines containing more than four deuterium atoms, and heavy bipyridyls, are formed. These characteristic features were attributed to processes which begin on heating and which involve and exchange of MgI residues from the organomagnesium compounds for the hydrogen of the pyridine and phenylpyridine:

$$C_6H_5MgI + C_5D_5N \rightarrow C_6H_5D + C_5D_4NMgI$$
$$C_5D_4NMgI + C_6H_5C_5D_4N \rightleftarrows C_5D_4HN + IMgC_6H_4C_5D_4N$$

and the formation of the bipyridyls was attributed to the reaction:



or to the addition of pyridyl radicals of thermal origin to pyridine.

These explanations were confirmed by the fact that the reaction between C_6H_5MgI and heavy pyridine at 120° gave the same products and isotopic compositions with the same characteristic features as in the reaction of C_6H_5I with magnesium.

The reactions of C_6H_5MgBr with $CoCl_2$, AgBr, $CuCl_2$, $PtCl_4$, $HgBr_2$, $FeCl_3$, $SnCl_4$, and $CrCl_3$ in a medium of heavy benzene mixed with ether were studied [117]. The published data on the mechanism of reactions of this type (for example Refs. 118–124) contain a number of contradictions. It was moreover not clear whether free radicals take part in the reactions.

The formation of free radicals was established in all these reactions, since they gave the benzenes-d_1 and -d_0 and biphenyls containing deuterium. Most of the biphenyls consisted of the d_0 form. In a number of instances their isotopic composition could not be explained without assuming the disproportionation of radicals of the hydrobiphenyl type, produced in intermediate stages of the formation of the biphenyls.

The source of the radicals was detected in experiments with $HgBr_2$ and $SnCl_4$, where the chief products were stable diphenylmercury and tetraphenyltin. It must be assumed that the radicals were obtained at the stage involving the formation of these organometallic compounds, since their decomposition did not take place. It is possible

that other organometallic compounds, which are assumed to be intermediate products of these reactions [118], are obtained by a free-radical mechanism. The decomposition of at least some of them [119-121,125] also probably involves radicals.

The fact that the d_0 form predominates in the biphenyls obtained in these experiments can be attributed to the fact that most of the biphenyls are obtained from phenyl residues which have not become free radicals. These radicals have combined in the reactive complex, in a "solvent cage" or on the surface of the metals. Only a small percentage of C_6H_5 residues were liberated, and these gave the deuterated biphenyls.

In the work cited it was also shown that the benzenes-d_1 and -d_0 are formed when a solution of C_6H_5MgBr in a mixture of heavy benzene and ether is heated to 50° or oxidised with atmospheric oxygen.

The participation of free radicals in the reactions of organic halides with alkali metals has not been extensively studied. The recently proposed [126] simple radical scheme:

$$ArX + M \rightarrow Ar^{\cdot} + MX;\ 2Ar^{\cdot} \rightarrow Ar - Ar \qquad (27)$$

cannot now be accepted, since it has been established that organometallic compounds are formed in intermediate stages of the Fittig reaction. The alternative scheme [127,128]

$$\text{a) } ArX + 2M \rightarrow ArM + MX$$
$$\text{b) } ArM + ArX \rightarrow Ar{-}Ar + MX \qquad (28)$$

does not exclude the production of radicals in the formation of organometallic compounds or in their reaction with the aryl halides [129]. Radicals were found in various examples of the Wurtz reaction [130,131], but not in the Fittig reaction [9,112].

The study of the reaction of lithium with fluorobenzene in heavy benzene [132,133] showed that the reaction gives the benzenes-d_1 and -d_0, and the ratio of the other forms of benzene remains unchanged. This proved the participation and reaction of $C_6H_5^{\cdot}$ radicals, since phenyl-lithium does not undergo isotopic exchange with benzene [134]. The participation of radicals was confirmed by the isotopic composition of the biphenyl, which was found to be characteristic for the free-radical mechanism (see sections II–IV). In heavy cyclohexane with heating, the benzenes-d_1 and -d_0, and biphenyl, are formed. Biphenyl is not obtained at 20°, so that the process stops at the stage of C_6H_5Li formation. Under these conditions also, the benzene-d_1 was not obtained.

These results show that $C_6H_5^{\cdot}$ radicals are produced by the reaction of C_6H_5Li with C_6H_5F, giving biphenyl, and not in the formation of C_6H_5Li.

The course of this reaction was represented by schemes (28*a*), of form (26) with the participation of C_6H_5Li and C_6H_5F, by the reaction:

$$2C_6H_5^{\cdot} \rightarrow C_6H_5{-}C_6H_5 \qquad (29)$$

and by schemes (3), (5), and (4), and also by analogous reactions of fluorobiphenyl, formed according to the last scheme.

The $C_6H_5^{\cdot}$ radicals obtained by a reaction of type (26), apparently recombine chiefly in a "solvent cage". Thus most of the biphenyl is of the d_0 form.

In the benzenes-(d_1 + d_0) the proportion of the benzene-d_1 is much less than that in other reactions involving $C_6H_5^{\cdot}$ radicals. This was explained by assuming that in addition to the usual routes, the benzene-d_0 is obtained by the reaction:

$$C_6H_5F + C_6H_5Li \rightarrow \langle\bigcirc\rangle + C_6H_6 + LiF\ . \qquad (30)$$

The study of the mechanism of the reaction of iodobenzene with sodium is complicated by isotopic exchange of phenylsodium with benzene [19,112]:

$$C_6H_5Na + C_6D_6 \rightleftarrows C_6H_5D + C_6D_5Na \qquad (31)$$

which, like the reactions of phenyl radicals, gives the benzene d_1. Analogous processes involving biphenyl distort its isotopic composition.

It has been shown [132,133], however, that after several hours at room temperature, without mixing, exchange is not observed, but that under these conditions in benzene, the d_1 and d_0 forms appear, and the ratio of the other forms remains unchanged, and in the biphenyl obtained the ratio of the isotopic forms is that characteristic for a radical mechanism. All this shows that the reaction involves $C_6H_5^{\cdot}$ free radicals. This conclusion was confirmed by experiments in heavy cyclohexane.

The reaction mechanism must be represented by schemes analogous to that assumed for the reaction of fluorobenzene with lithium. As in the experiments with lithium, the proportion of the d_1 form is unusually low in the benzenes-(d_1 + d_0) formed, and this was attributed to a reaction of type (30) involving iodobenzene and phenylsodium. The course of these processes has been convincingly proved [135].

These data show that the conclusion in Ref. 112 that the reaction of sodium with iodobenzene does not involve free radicals is incorrect.

It was stated above that the isotopic exchange of hydrogen between C_6H_5Na and C_6D_6 is not observed in the absence of mixing. This was attributed to the fact that benzene does not penetrate, or penetrates very slowly, into the thickness of the layer of phenylsodium and NaI surrounding the metal granules, or into the inner layers of the phenylsodium crystals. Thus exchange takes place only on the surface and remains insignificant. This interpretation is confirmed by the fact that mixing, which leads to mechanical breakdown of the above layer and to subdivision of the phenylsodium crystals, and also increase in the duration of contact between C_6H_5Na and C_6D_6, and heating, facilitate the exchange. The latter is observed from the appearance of deuterium in the benzoic acid obtained from phenylsodium and from the redistribution of deuterium (which often reaches random distribution) between the isotopic forms of benzene and biphenyl. The exchange of phenylsodium with benzene does not reach equilibrium, however, even under severe conditions, and part of the benzoic acid remains light. The other part consists of the set of isotopic forms corresponding to random distribution.

These observations confirmed the early assumptions [127,128,136,137] regarding the existence of the above layer, difficult to penetrate, on the surface of the sodium granules, and demonstrated the poor penetrability of the C_6H_5Na crystals with respect to benzene.

In the works cited [132,133], the reactions of fluorobenzene with sodium and potassium were also studied, and it was shown that they involve free radicals.

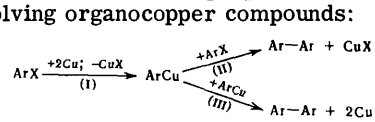
Subsequently, various examples of the Fittig and Wurtz reaction were studied [133-138] and it was found that a free-radical mechanism is extremely probable for the reaction of sodium with *p*-iodobiphenyl, α-iodonaphthalene, 9-iodophenanthrene, iodomesitylene, 2,4,6-triethyliodobenzene, 2,4,6-tri-isopropylbromobenzene, benzyl bromide, diphenylbromomethane, and triphenylchloromethane in heavy benzene or cyclohexane and for the reaction of sodium with ethyl iodide in a medium of heavy naphthalene. All these reactions gave hydrocarbons RD and RH corresponding to

the halides taken, and did not show signs of isotopic exchange between the compounds R–Na and the solvents; this exchange, like the reaction of R· radicals, might give RD molecules.

In the work cited it was also shown that the triphenylmethyl radicals, like many aryl and alkyl radicals, remove hydrogen from benzene. This reaction apparently involves an intermediate addition stage of the type corresponding to reactions (3).

In the interpretation of the mechanism of the reaction of aryl halides with copper (the Ulmann reaction) it was assumed that the halide forms on the metal surface a polar complex which attacks a second halide molecule [139,140], or that the reaction under the influence of copper gives free radicals, which react to give the final products [141,142], or, finally, that organocopper compounds are formed in some stages of the process [139]. Strong support was recently obtained for the last view.

The participation of radicals was proved [133,143] for the reaction of copper with iodobenzene, *p*-iodobiphenyl, and α-iodonaphthalene in a solution of heavy benzene or cyclohexane. The reactions gave benzenes, biphenyls, and naphthalenes-d_1 and -d_0, and the biphenyl isolated in the experiments with C_6H_5I in benzene had an isotopic composition corresponding to a free-radical mechanism of formation. The hydrocarbons (d_1 and d_0) obtained in benzene contained much more of the d_0 form than in other free-radical reactions. Here, as in the reaction of aryl halides with lithium or sodium, the hydrocarbons-d_0 are apparently formed not only from the usual sources of hydrocarbons-d_1 and -d_0 [reactions of types (3), (4), (5), and (11)], but also by reactions of type (30), which at the high temperature of the experiments (210–230°) become possible for organocopper compounds. The work cited adopted the scheme previously proposed [144] for the Ulmann reaction involving organocopper compounds:



(32)

with the refinement that stages I, II, or both involve the intermediate formation of aryl radicals. These processes apparently take place in such a way that only some of the radicals move from the surface into the solution. Thus the greater part of the diaryls formed does not contain deuterium. The reactions III probably take place in the reactive complex [144].

VIII. POSSIBILITIES AND LIMITATIONS OF THE METHOD

In conclusion we shall examine the extent to which the regular features of the behaviour of radicals and the criteria for a free-radical mechanism, discussed in this review, are of general importance.

These regular features and criteria were established for various hydrocarbon radicals—alkyl, aryl with different numbers of rings, arylalkyl (including such stable radicals as triphenylmethyl), and sterically hindered. It may be assumed that the great majority of hydrocarbon radicals show analogous behaviour. Differences in behaviour may be expected only for the radicals showing greatest steric hindrance (for example 2,4,6-tri-t-butylphenyl), since for these radicals, addition to aromatic rings and dehydrogenation and disproportionation of the addition products should be difficult. This is also to be expected for radicals which are unable to add on to aromatic systems for other reasons.

Dehydrogenation of type (11) may be brought about not only by R· radicals, but also by other radicals or oxidising agents X present in the system. As a result of this competition, the formation of the compounds RD may be suppressed by the preferential formation of the compounds XD, and one of the criteria for a free-radical mechanism is not observed. This possibility is apparently rarely realised, and was not observed in any of the works cited, even in the oxidation of hydrocarbons by chromyl chloride (section VI), when the concentration of the strong oxidising agent was high. The probability of complications of this kind is particularly great for R· radicals with low activity.

The formation of RD molecules may be prevented by the reaction of R· radicals with X· radicals produced simultaneously. This requires the collision of two short-lived species, however, and this process usually cannot compete with a reaction of type (11), in which R· adds on to the solvent, which is present in high concentration, and reacts with relatively stable radicals of the cyclohexadienyl type. The reaction of R· with X· (and the suppression of one of the criteria for a free-radical mechanism) may play a significant role in systems where the X· radicals have a low activity and their concentration is high.

Another complication is associated with the fact that disproportionation of type (1*b*) always competes with dehydrogenation of type (11) under the influence of R· radicals or other radicals or oxidising agents. A result of the competition may be the suppression of disproportionation. This leads to the non-observance of its consequences, for example a decrease in the concentration of d_5 form and an increase in the concentration of d_2 form in compounds of the type $R–C_6H_5$, formed by the reaction of R· radicals with benzene. Sections V and VII examined several examples of this kind, but it was shown that in these instances also, it is possible to reach reliable conclusions regarding the free-radical mechanism of reactions from the isotopic composition of the compounds of the form $R–C_6H_5$.

The suppression of disproportionation, as already noted, leads to the disappearance of the criteria for a free-radical mechanism proposed by Eliel and coworkers, since these are all consequences of the disproportionation.

It was shown above that most of the radicals which have been studied remove deuterium from heavy cyclohexane and the methyl group of heavy toluene, giving hydrocarbons RD (and RH). This criterion of a free-radical mechanism is convenient for the most reactive radicals, but not, for example, for benzyl radicals.

All the material of the present review shows that the method described for detecting free radicals and for studying the mechanism of free-radical reactions gives reliable results for a wide range of reactions with the participation of assumed participation of hydrocarbon radicals in solvents of different character. The applicability of this method to the study of radicals of other types has not yet been established.

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Pisarzhevskii Institute of
Physical Chemistry,
Academy of Sciences of the
Ukrainian SSR, Kiev

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Progress in the Chemistry of Primary Aliphatic Nitroamines

A.L.Fridman, V.P.Ivshin, and S.S.Novikov

Methods of making primary aliphatic nitroamines are considered. In addition to the well-known traditional methods for the preparation of nitroamines, little known methods for making them are examined and prospects for their further development are discussed.
This review is the first attempt in the world's literature to systematise the wealth of published material on primary aliphatic nitroamines. The literature is covered up to the end of 1967 or beginning of 1968. There is a bibliography of 207 references.

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I. INTRODUCTION

The progress in the chemistry of aliphatic nitro-compounds has stimulated interest in the nitroamines. This is shown by the large number of journal papers and patents published in recent years. The interest in the chemistry of aliphatic primary nitroamines arose not only because of the most interesting conversions of these compounds[1-3], but also the wide range of practical applications[4-11].

Isolated facts about the methods of preparation and properties of the primary aliphatic nitroamines can be found in monographs and review papers devoted to the nitro-compounds[1,12-14]. However, many of these papers are out of date or do not give sufficiently complete information about primary aliphatic nitroamines. There is no previous review paper on nitroamines in the Russian literature.

The present review surveys the published information on aliphatic primary nitroamines up to the end of 1967. In doing this the classical studies of Franchimont and his students and also other work on nitroamines carried out at the end of the last century is cited only where necessary and for the purpose of completeness in the material given. The early studies on nitroamines were surveyed more completely in 1912 by Baker[1].

Historically, two main periods can be distinguished in the development of the chemistry of the primary aliphatic nitroamines. The first began in 1888, when Franchimont synthesised methyl nitroamine[15,16], and continued for 20–25 years. This period is characterised by the appearance of fundamental studies on the nitroamines by such investigators as Franchimont[16-28], Klobbie[16,17,21,26], van Erp[27,29,30], Romburgh[31,32], Hantzsch[33-37], Baker[1,38,39], and others[40-45]. After 1915 until the nineteen-forties there was little interest in the nitroamines. But in 1948–1952 a long series of papers by Lamberton and coworkers[2,46-55] appeared, as well as interesting papers by Wright and coworkers[56-60], the work of McKay[61-74], and others[75-80]. Interest in nitroamines was reawakened and has not diminished since.

II. METHODS OF MAKING PRIMARY NITROAMINES†

Most of the known methods of making nitroamines can be divided into four groups: (1) the nitration of amines with preliminary protection of the amino-group; (2) the nitration of *N*-dichloroamines (Smart and Wright's method); (3) synthesis of nitroamines from nitroguanidine; and (4) direct nitration of amines by certain nitrating agents. There are also a few methods which at present are not of a general nature.

1. Nitration of Amines with a Previously Protected Amino-Group

Primary nitroamines, with rare exceptions, are readily decomposed by concentrated acids and cannot be obtained by the nitration of corresponding amines with nitric acid or its mixture with sulphuric acid. For the successful nitration of an amino-group it must first be protected. There are four main stages in the preparation of primary nitroamines by this method: (1) introduction of a protective grouping into the amino-group; (2) nitration of the protected amine; (3) removal of the protective grouping; and (4) isolation of the nitroamine.

Acetyl, formyl, oxalyl, alkoxycarbonyl, carbonyl, picryl, tosyl, and cyanoethyl groups can be used as the protective groupings.

The simplest of the primary nitroamines—methylnitroamine—was synthesised by the introduction of the oxalyl group into methylamine[21]:

$$CH_3NH_2 + (COCl)_2 \rightarrow (CH_3NHCO)_2 \xrightarrow{HNO_3} \left(\begin{array}{c} NO_2 \\ | \\ CH_3NCO \end{array}\right)_2 \xrightarrow{NH_3,\ ether}$$

$$\rightarrow \begin{array}{c} NO_2 \\ | \\ CH_3NH \end{array} \cdot NH_3 \xrightarrow{HCl} \begin{array}{c} NO_2 \\ | \\ CH_3NH. \end{array}$$

† Here and subsequently primary aliphatic nitroamines are being discussed, therefore the term "aliphatic" is often omitted.

The protection of amines by the oxalyl group is general and is used for the synthesis of a series of primary nitroamines and also of ethylenebisnitroamine[21,43,81]. The symmetric dialkyloxamides are readily nitrated with nitric acid or nitrating mixture. An example is the nitration of polynitroalkyloxamides[82-84]:

$$\begin{matrix}OCOC_2H_5\\OCOC_2H_5\end{matrix} + 2H_2NCH_2CH_2C(NO_2)_3 \rightarrow \begin{matrix}OCNCHH_2CH_2C(NO_2)_3\\OCNHCH_2CH_2C(NO_2)_3\end{matrix} \rightarrow$$

$$\xrightarrow{HNO_3+H_2SO_4} \begin{matrix}OCN(NO_2)CH_2CH_2C(NO_2)_3\\OCN(NO_2)CH_2CH_2C(NO_2)_3\end{matrix}.$$

The removal of the oxalyl group proceeds smoothly under the action of ammonia or boiling water.

Franchimont and his students[16,85] used an alkoxycarbonyl group as well as oxalyl as a protecting group in the nitration of amines. The method of preparing primary nitroamines through alkylnitrourethanes was subsequently perfected and developed and is now very important.

N-Alkylcarbamates are usually obtained by the reaction of esters of chlorocarboxylic acids with alkylamines in the presence of alkali[86]. However, often *N*-alkylcarbamates can also be obtained by other methods and they are more accessible than amines. A method of obtaining *N*-alkyl-*N*-nitrourethanes by the alkylation of nitrourethane with diazo-compounds or alkyl halides is interesting in this connection[55,87]:

$$\left.\begin{matrix}RCHN_2 + HN(NO_2)COOC_2H_5\\RCH_2Hal + AgN(NO_2)COOC_2H_5\end{matrix}\right\} \rightarrow RCH_2NCOOC_2H_5.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad NO_2$$

The production of various polynitroalkyl carbamates by the decomposition of azides of polynitrocarboxylic acids in the presence of alcohols, the reaction of isocyanates with alcohols, etc., has been described[88-96]:

$$RC(NO_2)_2CH_2CH_2CH_3 \xrightarrow{R'OH} RC(NO_2)_2CH_2CH_2NHCOOR' \xrightarrow{HNO_3+Ac_2O}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \rightarrow RC(NO_2)_2CH_2CH_2NCOOR'.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad NO_2$$

The nitration of *N*-alkylcarbamates is usually undertaken under the action of a sevenfold to fifteenfold excess of concentrated nitric acid[16,33,23,85,97]. Curry and Mason[98] proposed a mixture of acetic anhydride with nitric acid, which was more effective than nitric acid alone. This mixture nitrated many alkyl carbamates, including t-butyl carbamate, and also polynitroalkyl carbamates[89], whereas *N*-alkyl carbamates with branched alkyl residues are not nitrated by nitric acid[30]. An attempt to use tetranitromethane for the nitration of alkyl carbamates was unsuccessful[99].

The removal of an alkoxycarbonyl group is usually done under the action of ammonia in ethereal solution:

$$RNCOOC_2H_5 \xrightarrow{NH_3,\ ether} RNH\cdot NH_3 + C_2H_5OCONH_2.$$
$$\quad NO_2 \qquad\qquad\qquad\qquad\quad NO_2$$

Many alkylnitroamines and also ethylene-, trimethylene-, tetramethylene-, and pentamethylene-bisnitroamines were obtained by this method[16,85,100]. Hantzsch and Metcalf[33] obtained *N*-nitroglycine and some of its derivatives in a similar manner. Blomquist and Fiedorek[33] patented a method for making nitrates of nitroaminoalcohols of the type $C_2NOCH(R)CH(R')NHNO_2$.

It was subsequently shown that not only ammonia but also other amines are suitable for splitting *N*-alkyl-*N*-nitrourethanes and that the amination of *N*-alkyl-*N*-nitrourethanes is general and can be used to obtain the amine salts of primary nitroamines[99]. Hexamethylene-1,6-bisnitroamine was made in this way[99].

The hydrolysis of polynitroalkyl-*N*-nitrocarbamates has not been described. Such a study should give interesting information about the effect of electronegative groups on the ease of removal of alkoxycarbonyl groups.

Primary nitroamines are often obtained by the nitration of alkylureas. As long ago as 1888 Franchimont and Klobbie[17] nitrated imidazolid-2-one with nitrating mixture and then decomposed the 1,3-dinitroimidazolid-2-one with water to ethylenebisnitroamine:

$$\begin{matrix}H_2C-N\\|\\H_2C-N\\H\end{matrix}\!\!>CO \xrightarrow{HNO_3+H_2SO_4} \begin{matrix}H_2C-N(NO_2)\\|\\H_2C-N(NO_2)\end{matrix}\!\!>CO \xrightarrow{H_2O} \begin{matrix}NO_2\\|\\HN-CH_2-CH_2-NH\end{matrix}\!\!<\begin{matrix}NO_2\\|\\.\end{matrix}$$

Imidazolid-2-one can also be nitrated with nitric acid[101].

In nitration, monoalkylureas are readily converted into *N*-alkyl-*N'*-nitroureas; nitration of the nitrogen atom connected with the alkyl group does not usually take place[81]. An exception is methylurea, which is converted rather smoothly into *N*-methyl-*N*-nitrourea. The latter can be hydrolysed to methylnitroamine[39].

An interesting paper was recently published on the preparation of the first representative of the *N*-dinitroamine series—methyl-*N*-dinitroamine, obtained by the nitration of methylurea nitrate by a mixture of acetic anhydride and nitric acid[102]:

$$CH_3NHCNH_2\cdot HNO_3 \xrightarrow{HNO_3+Ac_2O} CH_3N(NO_2)(NO_2).$$
$$\quad\ O$$

In nitration, *sym*-dimethylurea is smoothly converted into *NN'*-dinitro-*NN'*-dimethylurea[103]. We note that the nitration of substituted ureas and their derivatives has not yet been sufficiently studied and further investigations in this field can lead to both the development of simple methods for making primary nitroamines and also to the preparation of other interesting compounds. This is shown by the above study by Japanese scientists[102] and also by other investigations[104-106].

The acetyl group is important as a protective group for the nitration of amines. Thus, one of the methods of obtaining ethylenebisnitroamine is based on the introduction of acetyl groups into ethylenediamine followed by the nitration of ethylenebisacetamide with a mixture of nitric acid and acetic anhydride[81]. The acetyl group is readily detached with water, alkali, or ammonia. Methylenebisnitroamine was obtained from methylenediamine in a similar fashion[47]. The synthesis of polynitroalkyl-*N*-nitroamines by the hydrolysis of polynitroalkyl-*N*-nitroacetamides is described in the patent literature[107-109].

Formyl groups are sometimes used instead of acetyl for the protection of amino-groups[110]:

$$H_2C(NHCHO)(NHCHO) \rightarrow H_2C(N(NO_2)CHO)(N(NO_2)CHO) \rightarrow H_2C(N(NO_2)H)(N(NO_2)H).$$

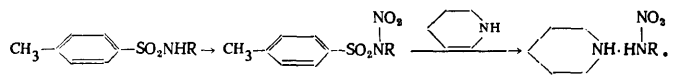
It is worth noting an extremely interesting method for obtaining *N*-alkylacetamides and *N*-alkylformamides, based on the condensation of the corresponding *N*-(hydroxymethyl)amides with nitroalkanes, for example, nitroform:

$$RCONHCH_2OH + HC(NO_2)_3 \rightarrow RCONHCH_2C(NO_2)_3 + H_2O.$$

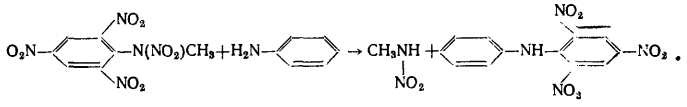
Unfortunately, the nitration of the trinitroethylacetamide and trinitroethylformamide thus obtained has not been described.

Gillibrand and Lamberton used a tosyl group for the protection of the amino-group[55]. The tosyl group is removed under rather severe conditions but the yields of the

primary nitroamines are reasonably high[111]. Piperidine is a convenient reagent for removing the tosyl group[111]:

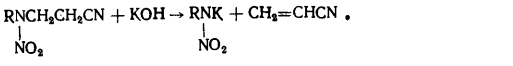


An example of the production of methylnitroamine by the removal of the picryl group from methylpicrylnitroamine under the action of aniline or *p*-toluidine has been described[1]:



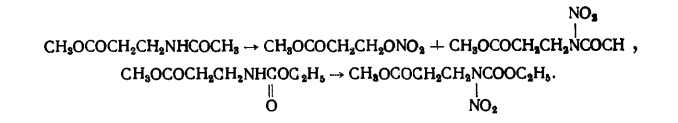
Since alkylpicrylnitroamines are readily obtained in the nitration of alkylanilines or dialkylanilines[12], the method of making primary nitroamines by using a protective picryl group opens up great possibilities.

Kissinger and Schwartz[112] observed the cleavage of 2-cyanoethylnitroamine in alkali into a salt of the nitroamine and acrylonitrile:

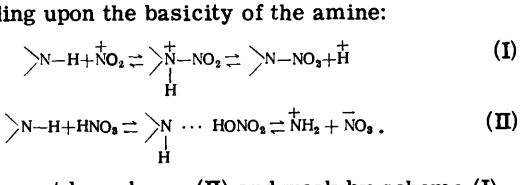


Although only one example of this reaction has been described, the readily accessible β-cyanoethylnitroamines, which are obtainable by the nitration of the corresponding aminonitriles[113,114], can probably serve as the initial compounds for obtaining primary nitroamines.

An analysis of the methods of preparation of primary nitroamines with protected amino-groups shows that the urethane method is the most universal, simplest, and most available at the present time. In every instance there are no indications in the literature of unsuccessful examples of the nitration of *N*-alkylcarbamates or of the removal of alkoxycarbonyl groups from *N*-alkyl-*N*-nitrocarbamates. In this connection it is interesting to compare the nitration of esters of glycine and β-alanine with the use of various protecting groups. Whereas nitration of the *N*-acetyl derivative of the methyl ester of β-alanine gives the *N*-nitroamide in insignificant yield the corresponding urethanes are nitrated quantitatively[115]:



The mechanism of the *N*-nitration of protected amines has not been discussed in the literature and there have not been systematic investigations in this field. A considerable drop in the basicity of the amine generally occurs on the introduction of the above protecting groups. It is well known that in the dialkylamine series strong bases without catalysts are not nitrated at the nitrogen atom, whereas amines of low basicity are nitrated rather readily[116]. Lamberton[2] considers that the reaction can proceed in two ways, depending upon the basicity of the amine:

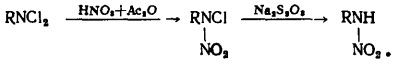


Strong bases react by scheme (II) and weak by scheme (I).

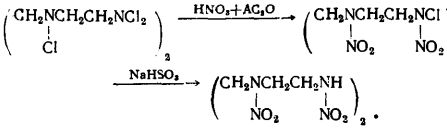
A protected amino-group is a weak base and its nitration can be described by scheme (I). The reversibility of the nitration is evidence for this scheme. It is known that *sym*-dinitrodimethyloxamide in sulphuric acid solution is a source of the nitronium cation and exhibits a nitrating action[117]. Similar examples have been given by Holstead and Lamberton[46].

2. Nitration of *N*-Dichloroamines (Smart and Wright's Method)

In 1948 Smart and Wright[56] proposed a new method for obtaining primary nitroamines. They found that on treatment of *N*-dichloroamines in an excess of acetic anhydride with concentrated nitric acid, chlorine is removed with the formation of *N*-chloro-*N*-nitroamines. In a reducing medium the latter lose a second chlorine atom and are converted into primary nitroamines:

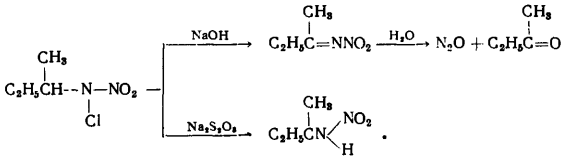


Butylnitroamine, isobutylnitroamine, n-octylnitroamine, ethylenebisnitroamine etc. have been obtained by Smart and Wright's method[56,57]. The example of *N*-hexachlorotriethylenetetramine has shown the possibility of the simultaneous substitution of nitro-groups for the chlorine atoms at primary and secondary nitrogen atoms[57]:

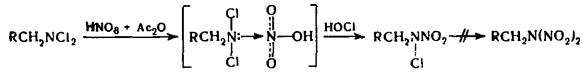


It is noteworthy that an intermediate *N*-chloro-*N*-nitroamine has been isolated in a pure form in only one instance, in small yield[56]. Nevertheless it is evident that *N*-chloro-*N*-nitroamines are more stable in acid than are primary nitroamines, which also ensures that the reaction will take place in the desired direction.

The replacement of a chlorine atom by hydrogen in *N*-chloro-*N*-nitroamines is effected under the action of aqueous solutions of alkalis, sodium hydrogen sulphite, or sodium thiosulphate[56,57]. When the product of the nitration of s-butyldichloroamine was treated with an aqueous solution of alkali the yield of s-butylnitroamine was only 10%, whereas sodium thiosulphate allowed the yield to be raised to 65%. It was thought[56] that depending upon the medium the intermediate *N*-chloro-*N*-nitroamine can be hydrolysed or can undergo intramolecular loss of hydrogen chloride[56]:



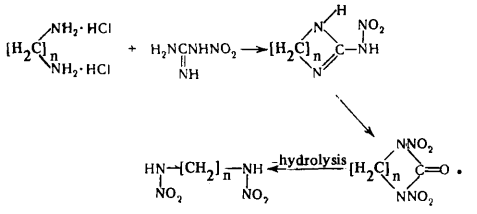
There has not been a thorough study of the mechanism of nitration of *N*-dichloroamines. In one of their papers[56] Smart and Wright suggested that nitric acid forms a complex with the *N*-dichloroamine, the nitrogen of the amino-group acting as a donor and the nitrogen of the nitric acid as an acceptor. The complex which is formed is unstable and readily loses hypochlorous acid to form an *N*-chloro-*N*-nitroamine. Because of the introduction of the nitro-group the *N*-chloro-*N*-nitroamine loses the donor properties and reaction cannot proceed further to form an *N*-dinitroamine:



3. Syntheses Based on Nitroguanidine

Nitroguanidine differs markedly from the primary nitroamines in its properties. Investigations in recent years [61] have shown that this compound should really be given a nitroimine structure. A review by McKay [14] dealt with the chemistry of nitroguanidine. The study of nitroguanidine derivatives has led to the discovery of new original methods of making primary nitroamines, which are also discussed in this section.

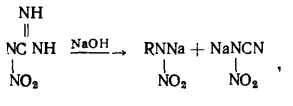
McKay and Manchester [62,63] developed a method for obtaining aliphatic bisnitroamines based on the nitration of the cyclic products of the interaction of diamines with nitroguanidine. The nitro-derivatives obtained are readily hydrolysed to the corresponding nitroamines:



1,2-Bisnitroaminopropane, 1,3-bisnitroaminobutane, and 1,3-bisnitroamino-2-nitroxypropane [62,63] were obtained in a similar manner.

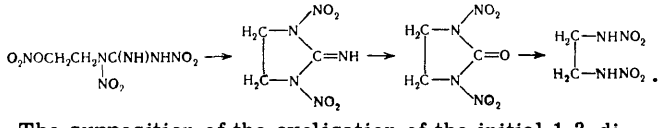
Primary nitroamines were obtained in many other instances. Thus in the cleavage of 2-amino-1-nitro-2-imidazoline a nitroamine salt is formed, the structure of which was proved by subsequent chemical transformations.

1-Alkyl-1,3-dinitroguanidines are split with alkali to salts of primary nitroamines and the extremely interesting, but little studied, cyanonitroamide [118]:



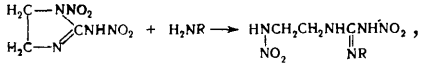
where R = CH_3 and n-C_4H_9.

The decomposition of 1,3-dinitro-1-(2-nitroxyethyl)-guanidine is extremely unusual. When this compound is boiled with water ethylenedinitroamine is isolated in 57% yield [118]:



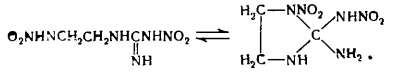
The supposition of the cyclisation of the initial 1,3-dinitro-1-(2-nitroxyethyl)guanidine is confirmed by the similar conversions of other *N*-(2-substituted ethyl)-*N'*-nitroguanidines [118].

In the interaction of 1-nitro-2-(nitroamino)imidazoline with ammonia or amines β-nitroaminoalkylnitroguanidines are formed [65,66,72,73]:



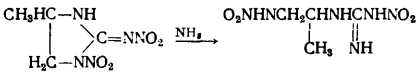
where R = H, CH_3, Ar.

Kirkwood and Wright [119] succeeded in showing that 1-nitro-2-(nitroamino)guanidine exists as two isomers. The position of the equilibrium is shifted to one side or the other depending upon the solvent:

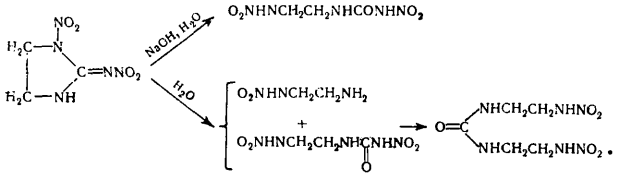


Later McKay [67] gave additional information in support of the existence of linear products.

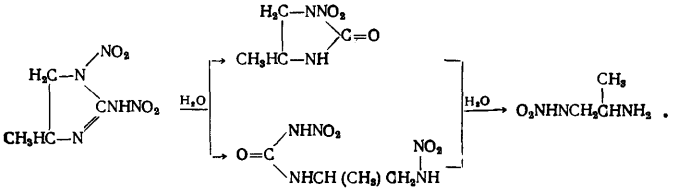
The difference in the opinions of these authors is evidently due to the ease of cyclisation and cleavage of the products of the addition of the amines to 1-nitro-2-nitriminoimidazolid-2-one. This circumstance makes difficult the hypothetical choice of any one structure. However, for certain compounds such a type of linear structure has been shown sufficiently clearly. For example, the product of the addition of ammonia to 4-methyl-1-nitro-2-nitriminoimidazolid-2-one is a linear primary nitroamine [68]:



When treated with alkali, 1-nitro-2-nitriminoimidazolid-2-ones are usually cleaved to primary nitroamines [69,70,120]. When 1-nitro-2-nitriminoimidazolid-2-one is hydrolysed with aqueous alkali, 3-nitro-1-(2-nitroaminoethyl)urea is obtained in good yield. The aqueous hydrolysis of this compound leads to bis-(2-nitroaminoethyl)urea as a result of the reaction of the primary decomposition products [121]:



Two products are also formed in the hydrolysis of 4-methyl-1-nitro-2-nitriminoimidazolid-2-one in water—*N*-2-(nitroamino)ethyl-1-methylnitrourea and 4-methyl-1-nitro-2-imidazoline, and on long boiling with water these are converted into 2-amino-3-nitroaminopropane [71]:



On dissolution in aqueous alkali, 1-nitro-2-propylamino-2-imidazoline is hydrolysed to *N*-2-nitroaminoethyl-*N'*-propylurea [120]. In an acid or alkali medium 1-nitro-2-*p*-acetamidophenylamino-1-nitro-2-imidazoline is hydrolysed to *N*-2-nitroaminoethyl-*N'*-pacetamidophenylurea [70].

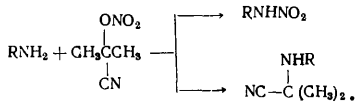
McKay and coworkers [74] described an interesting molecular rearrangement leading to the production of a primary nitroamine.

4. Direct Nitration of Amines

The relative complexity and multistage nature of the methods of synthesis of primary nitroamines are responsible for the search for new, simpler methods for their production. The most tempting was the direct nitration of primary amines.

From this point of view the method developed by Emmons and Freeman for the nitration of amines with acetone cyanohydrin nitrate 1-cyano-1-methylethyl nitrate is interesting [122]. Propyl, butyl, isobutyl, pentyl, and isopentyl nitroamines were obtained in 50–55% yield by this method. The reaction takes place under rather critical

conditions and is accompanied by the formation of aminonitriles:

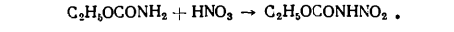


The method is suitable for the nitration of amines having bulky substituents at the α-carbon atom[122].

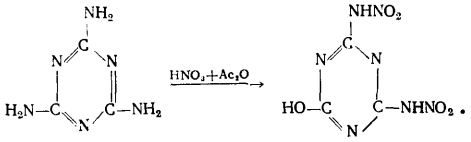
Another way of obtaining nitroamines was described recently in the patent literature. It is based on the reaction of nitryl fluoride with ammonia or amines in an inert solvent or in the vapour phase[123]. Information is available about the nitrating ability of nitrile chloride in relation to amines[124].

Primary nitroamines can also be obtained in the nitration of amines by acetyl nitrate in the presence of butyllithium[125]. The method is applicable only to compounds containing functional groups indifferent to butyl-lithium. Furthermore the complexity of the experimental conditions (low temperature, atmosphere of dry nitrogen) does not give this method a decisive advantage over the existing ones.

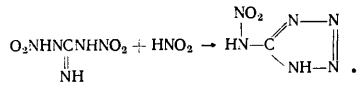
Although the methods of preparation and properties of nitroamides, which are similar in structure to the primary nitroamines, or those of aromatic and heterocyclic nitroamines are not discussed in the present review, we will note that some of these compounds can be obtained by the direct nitration of the corresponding amides and amines with nitric acid or nitrating mixture. Thus nitrourethanes are usually made by the nitration of urethane[47].



Benzosulphonitroamide and *p*-toluene sulphonitroamide are obtained in a similar fashion[126]. Aminopyridines are readily nitrated by nitrating mixture to the corresponding nitroaminopyridines[127]. The nitration of melamine with a mixture of acetic anhydride and nitric acid gives *NN'*-dinitroammeline[128]:



Triacetylmelamine gave nitroammelide. Under the action of nitrous acid, nitroaminoguanidine is converted into 5-nitroaminotetrazole[129,130]:

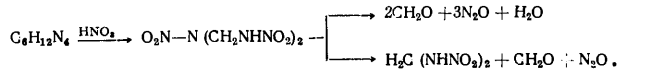


5. Other Methods of Preparation

The formation of nitroamines in the hydrolysis of linear products of the nitrolysis of tertiary amines has been described. Methylenebisnitroamine was first isolated as the barium salt from the pyrolysis products of hexamethylenetetramine[47].

2,4,6-Trinitro-2,4,6-triazaheptane-1,7-diol bistrifluoroacetate can be split by benzylamine to the corresponding amine salt of methylenebisnitroamine[131]. The hydrolysis of the linear products of the nitrolysis of Mannich bases also leads to the production of primary nitroamines[132].

The nitrolysis of hexamethylenetetramine is accompanied by the formation of a primary nitroamine as a side-product[133]. The latter is decomposed completely by hot water but under milder conditions it is hydrolysed to methylenebisnitroamine:

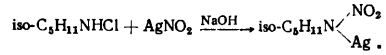


In reacting with nitric acid under mild conditions hexamethylenetetramine dinitrate forms 1,3-dinitro-1,3,5-triazapentane[134].

Freeman[135] obtained a series of nitroamines by the reduction of nitroimines with potassium tetrahydroborate or lithium tetrahydroaluminate. This work completed the discussion of the structure of nitroimines to which some investigators had ascribed the structure of pernitrosoketones.

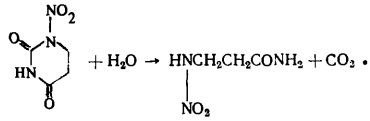
Examples are known of the production of primary nitroamines from the corresponding isodiazotates[136]. However, owing to the difficulty of obtaining the starting compounds this method is not widely used.

Finally, there is a single paper[137] on the production of a nitroamine in low yield by a reaction similar to the Wurtz reaction:



The preparation of primary nitroamines containing other functional groups in the alkyl residue is by the same methods as were given earlier. Naturally, the action of the functional group of the reagents employed for the preparation of the nitroamines must be considered. In particular, aminoalcohols are converted into the nitrates of the nitroaminoalcohols[19,138]. However, under certain conditions the nitrate group can be removed or its formation avoided completely[138,139].

Nitroaminoacetamide is obtained when nitrohydantoin is boiled in water for a long time[92]. Nitroaminopropionamide can be obtained from nitrohydrouracil[20]:



Free nitroaminocarboxylic acids are formed in the hydrolysis of amides with alkali. δ-Nitroaminovaleric and ϵ-nitroaminocapronic acids are obtained in the alkaline hydrolysis of the corresponding *N*-nitrolactams[140]. Propargylnitroamine is obtained by the usual scheme by the nitration of *N*-propargylurethane[141].

III. PHYSICAL PROPERTIES AND STRUCTURE

1. General Characteristics

Primary aliphatic nitroamines are liquids or readily melting crystalline compounds. The first member of the homologous series of monoalkylnitroamines—methylnitroamine—melts at 38°C,[16] ethylnitroamine at 6°C,[16] and the higher homologues are also low-melting or liquid substances. The bisnitroamines are solids whose melting points depend on the number and multiplicity of the methylene groups in the molecule.

Primary nitroamines are weak acids. Thus the pK_a of methylnitroamine is 6.0;[142] its homologues are even

weaker acids. When electronegative groups are introduced into the alkyl chain of the nitroamine the acidic properties increase. The dissociation constants of $\alpha\omega$-bisnitroamines have been determined[143]. A comparison of the pK values obtained with those for $\alpha\omega$-dicarboxylic acids shows that with increase in the number of methylene groups the difference between the first and second dissociation constants decreases in the bisnitroamine series more slowly than in the dicarboxylic acid series (Table 1).

Table 1. Dissociation constants of $\alpha\omega$-dinitroamines and $\alpha\omega$-dicarboxylic acids (20°C).

α,ω-Bisnitroamines	pK_1	pK_2	ΔpK	Acid	pK_1	pK_2	ΔpK
Methylene	5.0	6.6	1.6	Malonic	2.83	5.69	2.86
Ethylene	5.35	6.66	1.31	Succinic	4.22	5.67	1.45
Trimethylene	5.59	6.85	1.26	Glutaric	4.39	5.50	1.11
Tetramethylene	5.87	6.98	1.11	Adipic	4.43	5.49	0.95

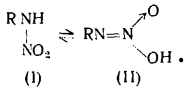
Baly and Desch studied the optical properties of the nitroamines[144]. They showed that the unsubstituted alkylnitroamines have normal molecular refraction.

The use of primary nitroamines as explosives stimulated the study for some of them of the thermochemical, stability and explosive characteristics. The information on these characteristics has been surveyed in Orlova's monograph[145]. Primary nitroamines are relatively stable thermally, the liquid compounds can be distilled under vacuum, and the thermal stability of the crystalline nitroamines is different. Methylenebisnitroamine is of low thermal stability, whereas ethylenebisnitroamine is distinguished by high stability, has good explosive characteristics, and diminished sensitivity to shock[146]. A differential thermal analysis of nitroamines was recently made[147]. Medard determined the heats of formation of ethylenebisnitroamine (25.65 kcal mole^{-1}) and nitroaminoethyl nitrate (45.8 kcal mole^{-1}).[148]

The physiological activity of the primary nitroamines has hardly been studied. There is information on the comparative physiological action on the human organism of nitromethane and methylnitroamine[149]. When the latter is introduced into the human organism it does not produce any changes in the composition and pressure of the blood, that is, unlike nitrates and nitroalkanes it is harmless for man. It was also noted that ethylenebisnitroamine has no harmful action on the human organism[12].

2. Structure and Spectra

The aliphatic nitroamines were first ascribed the structure of the true N-nitro-compounds (I). Later, Hantzsch[34-37] by starting from a formal analogy between the nitroalkanes and primary nitroamines, suggested that the latter exist in two tautomeric forms:



(I) (II)

By this scheme he explained the acidic properties of nitroamines and the formation of O-isomers in the alkylation of the salts of nitroamines. Hantzsch attempted to confirm this concept of tautomerism in a series of nitroamines by physicochemical methods. The evidence in support of tautomerism was that he observed an arrest (the time needed for the displacement of the equilibrium I⇌II) in the precipitation of the ammonium salt of the nitroamine on passing ammonia through a solution of the nitroamine in benzene. Furthermore, he observed a high temperature coefficient of electrical conductivity for salts of the nitroamine in aqueous solution. However, Euler showed[44] that these results cannot serve as proof of the tautomerism of the primary nitroamines.

Thorough physicochemical investigations made recently allowed the nature of the primary nitroamines to be more deeply understood. X-Ray structural analysis of ethylenebisnitroamine showed that the nitro-group in this compound exhibits normal properties, that is, the valence angles are similar to the angles of the nitro-group of p-dinitrobenzene, and the interatomic distances N–O (1.23 Å) in the nitroamine group are equal and comparable with the values for nitromethane[79]. Hence the conclusion that the structure of true N-nitro-compounds is more probable in the un-ionised form for the primary nitroamines. In addition there is a considerable shortening of the C–N and N–N bonds in comparison with the sum of the covalent radii (1.41 and 1.33 Å in comparison with 1.47 and 1.40 Å), and it is concluded that there is an electronic displacement from the nitrogen connected to the nitroamine group leading to the formation of a positive charge, which decreases the radius of the simple (N–C) bond of the nitrogen. The short N–N bond has 15% of the character of a double bond.

The X-ray structural method does not allow the location of the hydrogen atom in primary nitroamines to be determined. More reliable information on this aspect is obtained as a result of the spectroscopic analysis of nitroamines.

A study of the infrared spectra of a series of nitroamines showed that asymmetric vibrations in the range 1630–1550 cm^{-1} range and symmetric vibrations in the 1354–1262 cm^{-1} range are characteristic of the nitro-groups in these compounds. When there are electronegative substituents in the nitroamines the asymmetric vibrations are shifted to the side of higher frequencies[78,150,151]. The band in the 1000–948 cm^{-1} range is assigned to the vibrations of the N–N bond.

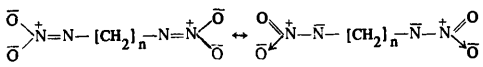
The complexity of the infrared spectra of the primary nitroamines in the 3600–3000 cm^{-1} range required additional confirmation that the bands in this region belong to the vibrations of the NH group. This information was obtained in a thorough study of the infrared spectra of crystalline ethylenebisnitroamine and tetramethylenebisnitroamine and their N-deuteriated analogues[152]. A comparison of the spectra of these nitroamine and their N-deuteriated derivatives allowed the 3240 and 3253 cm^{-1} bands observed in the spectra of ethylenebisnitroamine and tetramethylenebisnitroamine to be assigned to the stretching vibrations of the NH bond which participates in the formation of a hydrogen bond with the nitro-group of a neighbouring molecule in the crystal. In the spectra of the N-deuteriated nitroamines these bands are shifted into the 2400 cm^{-1} region. Bands characteristic for the asymmetric and symmetric stretching vibrations of the CH_2 group appear, which were masked earlier by the intense vibrations of the NH groups. In the spectra of the deuteriated analogues of the nitroamines studied there is also a displacement of the bands assigned to the asymmetric vibrations of the nitro-group, etc.

Hence the infrared spectra also confirm the true nitroamine structure of the primary nitroamines, at least in the un-ionised state.

The ultraviolet spectra of the primary nitroamines have been studied [78,153,155]. A maximum at 232 nm (235 nm in alkaline medium) is characteristic for methylenebisnitroamine in this range. In an alkaline medium there is a bathochromic shift of the maximum [78].

The Raman spectra of the primary nitroamines were studied by Kohlrausch and Wittek [156].

In discussing the structure of the primary nitroamines reference must again be made to the work on the determination of the dissociation constants of the $\alpha\omega$-bisnitroamines (Table 1). Since ΔpK decrease more slowly in the bisnitroamine series than in the dicarboxylic acid series, it was concluded that the effective distance between the charges of the double anions increases more slowly in the bisnitroamine series [143]. In this paper the ionised bisnitroamines are regarded as mesomeric anions. It is thought that the contribution of structure (III) is more characteristic for methylenebisnitroamine than for tetramethylenebisnitroamine.

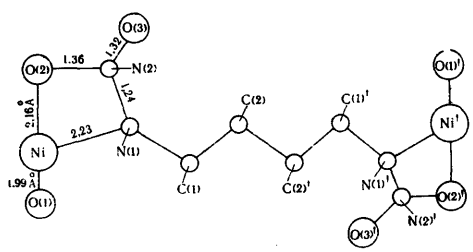


(IV)

It was recently suggested that the lower thermal stability of the primary nitroamines and their salts in comparison with secondary nitroamines is due to the conversion of the primary compounds into the aci-form on heating. Compounds in an aci-form are less stable and easily decompose [147]. However, experimental proof in support of this view has not been forthcoming.

Several studies deal with the explanation of the structure of salts of nitroamines by physicochemical methods. On the basis of an X-ray diffraction analysis of the disodium salt of ethylenebisnitroamine Alentoff and Wright maintain that the anionic centre in this compound is the oxygen atom and not the amine nitrogen [59]. However, the authors think it undesirable to attribute the structure found in a particular example to all the salts of the nitroamines with alkali metals, considering that the compound they investigated could be exceptional owing to the unique symmetry of the anion. Subsequent investigations showed that the salts of the nitroamines have a more complex structure.

In an X-ray diffraction study of the hydrate of the nickel salt of tetramethylenebisnitroamine it was found that in the crystalline state this compound exists in the form of polymeric chains. Each molecule of the ligand joins two nickel atoms with coordination of both nitroamine groups. The nitroamine group acts as a chelate ligand. The oxygen atom (Ni–O 2.16 Å) and the amine-nitrogen atom (Ni–N 2.23 Å) are coordinated so that a four-membered ring is formed with the nickel atom and the other nitrogen atom [157].



It is interesting that the study of the Raman spectra of the potassium salts of methyl- and ethylnitroamines showed that they have the structure of true *N*-nitrocompounds [156]. As already noted, on going from a free nitroamine to its salt there is a displacement of the maximum in the ultraviolet spectrum [78]. A difference was also noted in the infrared spectra of the primary nitroamines and their salts. This all suggests that the nitroamine anion should be regarded as a mesomeric anion with reaction centres at oxygen and nitrogen

IV. CHEMICAL PROPERTIES

The primary nitroamines exhibit high reactivity, which is in many respects similar to that for mono- and polynitroalkanes. Their activity is due to the presence of the labile hydrogen atom of the primary nitroamino-group and also to the nitroamino-group itself. Owing to the labile hydrogen the nitroamines form salts which undergo condensation with formalin‡, the Mannich reaction, add to activated double bonds, are alkylated, etc.

1. Reaction with Bases

Primary aliphatic nitroamines are weak acids and are capable of forming salts with bases. To obtain salts of nitroamines, bases, or metal oxides, carbonates, or alkoxides are used [1]. Potassium, barium, cobalt, zinc, copper, nickel, silver, mercury, lead, ammonium, and many other salts of primary nitroamines are known. In the preparation of salts of nitroamines in water, hydrates are often formed with various water contents in the molecule. Some metal salts of nitroamines are decomposed by boiling water. However, they are usually thermally more stable than the initial nitroamines but more sensitive to shock. In this respect the silver and mercury salts of the nitroamines are especially dangerous. Nitroamine salts are often used for the purification and analysis of nitroamines and also in certain chemical changes.

It is generally accepted that the primary nitroamines are stable in an alkaline medium. The anions of the aliphatic nitroamines do not react with a hot 20% solution of potassium hydroxide and only very concentrated alkali under severe conditions can bring about the decomposition of the primary nitroamines [29,30]. However, Hantzsch long ago observed [33] the decomposition of nitroaminoacetic acid and its derivatives by alkali under relatively mild conditions. These experiments were subsequently reproduced and analysed [51]. It was observed that some primary nitroamines, particularly those with electronegative substituents in the alkyl residue, are capable of decomposition by the scheme

$$RR'CHNHNO_2 \rightarrow RR'C{=}O + N_2 + H_2O$$

under the action of dilute alkali on heating.

Decomposition by this reaction is assisted by an increase in the hydroxide ion concentration, an increase in the concentration of sodium or potassium ions, and an increase in the electrical conductivity of the grouping in the alkyl residue. Furthermore, the presence of hydrogen at the α-carbon atom is important. Compounds without hydrogen in the α-position are stable to alkalis.

‡ Attempts to carry out condensation with other aldehydes were unsuccessful [24].

2. Reactions with Acids

Long ago Franchimont and coworkers[25,31,158] observed that primary nitroamines are decomposed by aqueous sulphuric acid with the formation of dinitrogen oxide and an alcohol:

$$RNHNO_2 \rightarrow ROH + N_2O.$$

Subsequent study of this reaction showed that it is more complex. During acid hydrolysis tetramethylenebisnitroamine forms butadiene and tetramethylene oxide in addition to dinitrogen oxide and butanediol. In the decomposition products of hexylnitroamine there are dinitrogen oxide, hexene, primary and secondary hexyl alcohols, and dihexyl ether[30]. Acetaldehyde was observed in the decomposition products of ethylenebisnitroamine[31].

On the basis of the results obtained in the acid decomposition of primary nitroamines and bisnitroamines it was suggested that the reaction proceeds through the intermediate formation of nitroamide and a carbonium ion[49]:

$$RNHNO_2 + H^+ \rightarrow R^+ + NH_2NO_2.$$

Nitroamide is the source of the dinitrogen oxide and water and the extremely active carbonium ion is stabilised with the formation of an alcohol (reaction with water), alkene (loss of a proton), or other decomposition products as a result of the reaction with nucleophilic reagents present in the reaction sphere.

The reaction of nitroamines with acids is regarded as an electrophilic substitution of the S_E2 type at the amine-nitrogen. The rate of reaction is directly proportional to the concentration of protons and of the primary nitroamine. The accumulation of electron-donating substituents at the nitrogen facilitates the decomposition of the nitroamines.

Further study of the acid decomposition of primary nitroamines was by the example of alkyl derivatives with a branched chain[50]. Such compounds decompose more rapidly than alkylnitroamines of linear structure and furthermore a definite difference in their behaviour in relation to sulphuric and hydrochloric acids is observed at the same pH. The decomposition of isopropyl nitroamine is catalysed by hydrogen sulphite ions.

In one study[50] the hypothesis about the formation of nitroamide at the first stage of acid hydrolysis has been doubted. Hence although there is a definite relation between the rate of decomposition of the primary nitroamines and the concentration of hydrogen ions the reaction is extremely complex and has still not been properly studied. The reaction of primary nitroamines with hydrochloric acid takes place rather smoothly with the formation of alkyl chlorides[49]:

$$RNHNO_2 + HCl \rightarrow RCl + N_2O + H_2O.$$

This is widely used for confirming the structure of the primary nitroamines[62,74,121,159]. The reaction of primary nitroamines with acetyl chloride and thionyl chloride proceeds similarly[14,58].

Primary nitroamines are extremely sensitive to nitric acid. Methyl nitroamine is decomposed by concentrated nitric acid even at 0°C with the formation of methyl nitrate and dinitrogen oxide[1]. Nitrous acid also readily decomposes methylnitroamines in aqueous solution to methanol, dimethylnitroamine and its *O*-isomer[23]. It was suggested that the decomposition proceeds through the intermediate formation of diazomethane[23]:

$$CH_3NHNO_2 + HNO_2 \rightarrow CH_3N{=}NOH + HNO_3,$$
$$CH_3N{=}NOH \rightarrow CH_2N_2 + H_2O,$$
$$CH_3NHNO_2 + CH_2N_2 \rightarrow (CH_3)_2NNO_2 + CH_3N{=}\overset{\overset{O}{\nearrow}}{N}{-}OCH_3.$$

3. Oxidation and Reduction

There has been almost no investigation of the reaction of primary aliphatic nitroamines with oxidants. There is only the statement that primary nitroamines are rather stable to oxidants[1].

The reduction of nitroamines has been studied in greater detail. When reduced with zinc in acetic acid methylnitroamine is converted into methanol, and when reduced with sodium amalgam methylamine is formed[18]; methylhydrazine is liberated by the action of zinc in nitric acid. An alkaline solution of aluminium converts methylnitroamine into methylisodiazotate[161]. In the reduction of ethylenebisnitroamine by zinc in hydrochloric acid a little ethylhydrazine is liberated[160]. It is suggested that the reduction of nitroamines proceeds through the intermediate formation of nitroso-derivatives which are readily isomerised into diazo-compounds. The latter can be isolated from alkaline solutions as diazotates.

4. Reaction with Formaldehyde

One of the characteristic reactions of primary nitroamines is their reaction with formaldehyde. Franchimont[24] first observed this reaction in the presence of bases. It was shown later that bisnitroamines readily form the corresponding nitroaminocarbinols on reaction with formaldehyde[75]:

$$[H_2C]_n(NHNO_2)_2 + CH_2O \xrightarrow{H_2O} [H_2C]_n(N(NO_2)CH_2OH)_2.$$

Only the monomethyl derivative could be isolated for ethylenebisnitroamine[75,81]:

$$O_2NHN{-}[CH_2]_2{-}NHNO_2 + CH_2O \xrightarrow{H_2O} HOCH_2\overset{\overset{NO_2}{|}}{N}{-}[CH_2]_n{-}\overset{\overset{NO_2}{|}}{N}H.$$

The mechanism of formation and the chemical nature of the hydroxymethyl derivatives was thoroughly studied with the aid of potentiometric titration and the analytical determination of formaldehyde[52]. It was shown that the hydroxymethylnitroamines dissociate readily in water with the loss of formaldehyde

$$RNCH_2OH \rightleftharpoons RNH + CH_2O.$$
$$\quad\;|\qquad\quad\;|$$
$$\quad NO_2\qquad NO_2$$

The position of the equilibrium is displaced to the right. Aqueous solutions of the dicarbinol derivatives of ethylenebisnitroamines and trimethylenebisnitroamine can be accurately titrated with potassium hydroxide as free nitroamines; the combined formaldehyde is also readily determined by well known procedures[52].

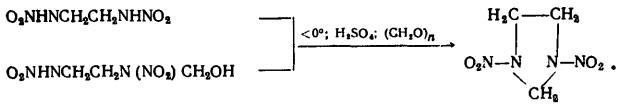
The hydroxymethylenebisnitroamines are more stable in acid solutions, since the electron-withdrawing properties of the nitroamino-group hinder the dissociation of the hydroxyl. Here the loss of a proton seems more hypothetical[52]:

$$RNCH_2OH \rightleftharpoons RNCH_2O^- + H^+.$$
$$\quad\;|\qquad\quad\;|$$
$$\quad NO_2\qquad NO_2$$

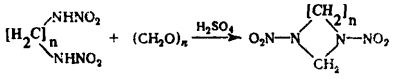
The interaction of nitroamines with paraformaldehyde in organic solvents also leads to the formation of nitroaminocarbinols. In sulphuric acid medium at low temperature methylenebisnitroamines are formed[162]:

$$RNH + [CH_2O]_n \xrightarrow{H_2SO_4} RNCH_2NR.$$
$$\quad\;|\qquad\qquad\qquad\quad\;|\qquad\;|$$
$$\quad NO_2\qquad\qquad\qquad NO_2\;NO_2$$

Ethylenebisnitroamine and its hydroxy-derivative form 1,3-dinitro-1,3-diazacyclopentane under these conditions[162]:

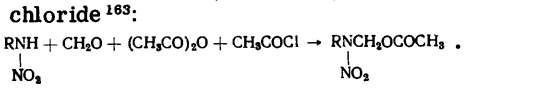


The higher homologues of ethylenebisnitroamine—trimethylenebisnitroamine and tetramethylenebisnitroamine—form 1,3-dinitro-1,3-diazacyclohexane and 1,3-dinitro-1,3-diazacycloheptane respectively in this reaction[80]:



where n = 3 or 4.

In research practice instead of the carbinol hydroxymethylnitroamines their derivatives are often used—acetates, nitrates, and chloromethylnitroamines[163]. The acetates of the nitroaminomethylols are obtained by the direct reaction of nitroamine, formalin, acetic anhydride, and acetyl chloride[163]:

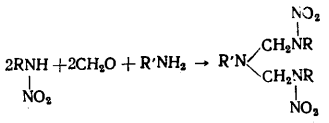


The nitrates of the hydroxymethylnitroamines, which exhibit an alkylating action, are usually of low stability and dangerous to use[164]. Important derivatives of the hydroxymethylnitroamines are the recently discovered *N*-(chloromethyl)-*N*-nitroamines, the chlorine atom of which has a reactivity reminiscent of the chlorine in chloromethyl ethers and is capable of replacement by various functional groups[164].

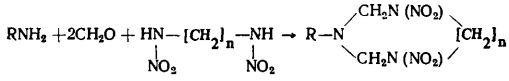
5. Aminomethylation of Primary Nitroamines

The possibility of using the primary nitroamines in a Mannich reaction was first demonstrated by the example of the reaction of methylnitroamine with *N*-hydroxymethylpiperidine[24]. Ammonia was investigated, as well as piperidine, as the amino-component, and methyl-, ethyl- and ethylenebis-nitroamines were also studied as the N–H acid component[25].

In the last 20 years there has been a thorough study of the Mannich reaction in a series of nitroamines. In 1949 Chapman and coworkers showed that for primary amines both of the hydrogen atoms of the latter take part in the condensation[165]:

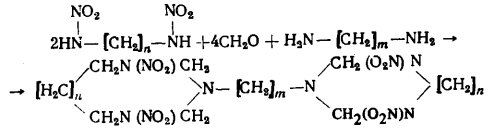


$\alpha\omega$-Bisnitroamines with not more than three methylene groups in a chain form cyclic condensation products[165]:



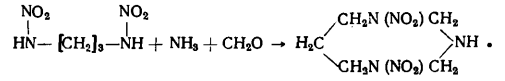
where n = 1–3.

Bicyclic compounds are isolated in the example of diamines[165]:

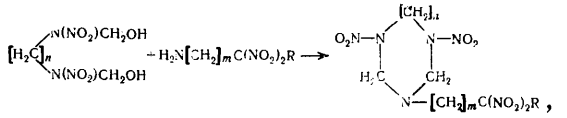


where n = 1–3, m = 2.

The formation of a bicyclic product was also observed in the condensation of ethylenebisnitroamine with ammonia and formalin (n = 2, m = 1)[166], but for trimethylenebisnitroamine a monocyclic product is formed as well as the bicyclic product (n = 3, m = 1)[80]:

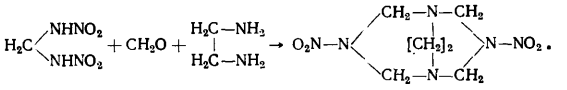


An interesting example of cyclisation was observed in the condensation of bisnitroaminodiols with polynitroalkylamines[167–170]:

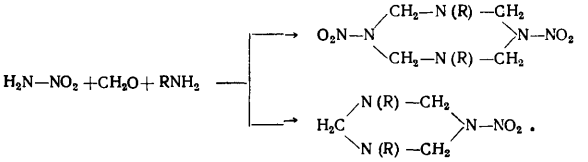


where n = 1 or 2, m = 2–6, R = NO_2 or CH_3.

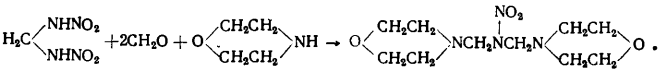
Quite recently[171–173] a new series of studies appeared on the condensation of dinitramines—$O_2NHN[CH_2]_nNHNO_2$, n = 1–4—with formaldehyde and diamines—$H_2N[CH_2]_nNH_2$, n = 2, 3, 4, 6—and also methyl-, ethyl-, butyl-, 2-hydroxyethyl-, hydroxypropyl-, trinitropropyl-, and benzylamines, aniline, phenylenediamine, 3,3-dinitropentamethylene-1,5-diamine, 3,6-dinitro-3,6-diazaoctamethylene-1,8-diamine, bis-2-aminoethyl ether. From a large amount of experimental material it was shown that the basicity of the amines and diamines in the aminomethylation of ethylenebisnitroamine has no effect on the nature of the reaction products. The more basic the amino-component introduced into the reaction the higher the pH of the medium at which formation of the cyclic products takes place. Special attention was paid to the behaviour of methylenebisnitroamine in the Mannich reaction. On reaction with ethylenediamine and formaldehyde at pH 4.6–5.6 it forms 3,7-dinitro-1,5-*endo*-ethylene-1,3,5,7-tetra-azacyclo-octane:



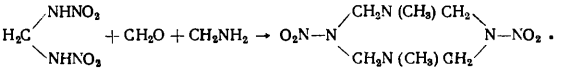
N-Nitroamide is the only nitro-derivative which contains two hydrogen atoms at the nitrogen carrying a nitro-group, therefore the aminomethylation of this compound can proceed in two directions:



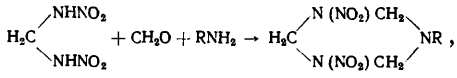
Methylenebisnitroamine is often used as a source of nitroamide, and depending on the conditions of carrying out the Mannich reaction it can function as a bisnitroamine or as a nitroamide[165]. The reaction of methylenebisnitroamine with morpholine and formaldehyde in water or ethyl acetate is:



The formation of derivatives of nitroamide was also observed in an anhydrous medium in the reaction with methyl-, benzyl-, and cyclohexylamines.

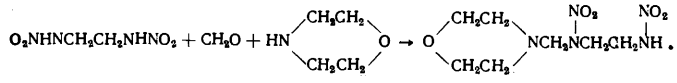


In aqueous medium products are obtained which contain the structural of methylenebisnitroaminemoiety [165].



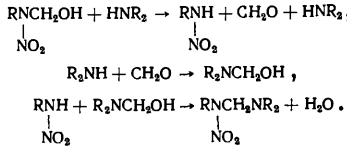
where R = CH_3, $C_6H_5CH_2$.

Linear Mannich bases are formed in the condensation of ethylenebisnitroamine with formaldehyde and morpholine [75]:



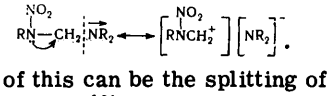
With two moles of formaldehyde and morpholine the reaction proceeds at two nitroamine groups [75].

The mechanism of the aminomethylation of the primary aliphatic nitroamines has been insufficiently studied. Lamberton and coworkers [52] proposed the following reaction scheme:

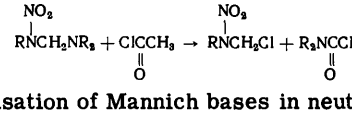


Under the action of alkalis Mannich bases are readily decomposed into nitroamine salts, amines, and formaldehyde; in an acid medium their stabilisation with the formation of the cation $RH(NO_2)CH_2N^+HR_2$ is possible [52].

It is interesting that the Mannich bases obtained from nitroalkanes (especially the mononitroalkanes) differ sharply in their chemical behaviour from the products of the aminomethylation of the primary nitroamines [52]. The former, as is well known, are insoluble in water, readily soluble in organic solvents; they cannot be titrated with alkali. The latter are readily titrated with alkali and soluble in water and other polar solvents. The reason for such a marked difference must, we think, be sought in the mutual influence of the nitroamine and amino-groupings at a single carbon atom. Like *N*-(chloromethyl)nitroamines, where the chlorine exhibits considerable lability on account of the $+M$ effect of the nitrogen atom and the I effect of the chlorine atom, the $+M$ effect of the amine-nitrogen of the nitroamino-group is evidently due to the stabilisation of the carbonium ion:



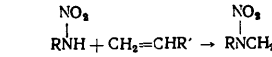
Confirmation of this can be the splitting of the Mannich bases by acetyl chloride [164]:



The polarisation of Mannich bases in neutral media is due to their preferential solubility in polar solvents and their ready cleavage by alkalis into their components.

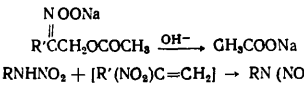
6. Addition at an Activated Double Bonds

Despite the fact that the addition of primary nitroamines to compounds which contain activated double bonds, found in the initial stages of the study, interesting results in this field were also obtained recently. This reaction was first found by Kissinger and Schwartz [112]. The alkenes studied were methyl acrylate, acrylonitrile, acrylamide, methyl vinyl ketone, and diethyl maleate; the nitroamines chosen were methyl-, ethyl-, and butyl-nitroamines and also ethylenebisnitroamines and *N*-methylethylenebisnitroamines. The reaction takes place only in the presence of an alkaline catalyst:

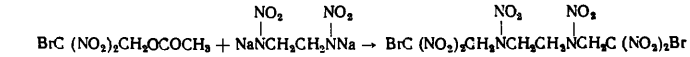


The addition of ethylnitroamine to 2,2-dinitropropanediol acrylate [174] takes place similarly.

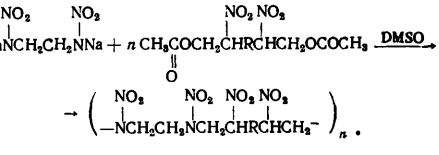
Nitroamines are capable of adding to a double bond of nitroalkenes and unsaturated ketones [175,176]. The reaction with nitroalkenes can also take place at the moment of their liberation from nitroalkyl acetates [177]:



An interesting example is the bromodinitroethylation of the alkali salts of nitroamines. In the first stage the reaction proceeds by the cleavage of bromodinitroethyl acetate into *gem*-dinitroethylene and sodium acetate. Subsequently the excess of the nitroamine salt adds to the dinitroethylene to form the corresponding salt of dinitroethylenetriamine. Under the action of a bromonium ion the latter is converted into the corresponding bromo-derivative [178].



The addition of $\alpha\omega$-dinitroamines to the decomposition products of acetates of nitrodiols leads to the formation of polymeric products [179]:



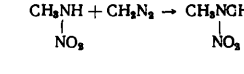
Polymers of high molecular weight are formed on carrying out the reaction in solvents indifferent to an activated double bond. When water, alcohols, or nitro-compounds are used as solvent the chain is broken owing to the addition of solvent molecules at the double bond.

7. Alkylation and Acylation

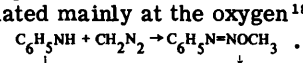
The alkylation of primary nitroamines is important for finding the structure of nitroamines and their salts and also for the synthesis of secondary nitroamines. In studying these reactions even the first investigators found that in alkylation often a mixture of isomers is formed, the quantitative composition of which depends on the nature of the alkylating agent, the metal cation, and the medium in which the reaction is carried out.

Alkylation of diazoalkanes. The reaction of primary nitroamines with diazoalkanes is of interest from the standpoint of finding the structure of nitroamines by chemical means.

In the treatment of nitroamide with diazomethane the main reaction product is dimethylnitroamine [180]. The latter is also obtained in quantitative yield in the alkylation of methylnitroamine [181]:



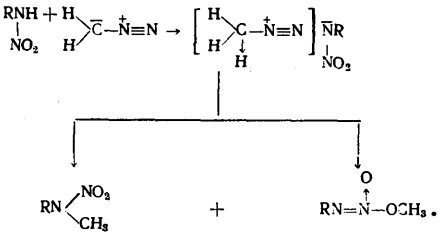
It is interesting to note that the more acid phenylnitroamines are alkylated mainly at the oxygen[181]:



In the alkylation of primary nitroamines with diazoethane ethyl derivatives are formed[57].

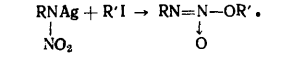
In the examples described above the investigators usually either did not note the formation of isomeric products of *O*-alkylation, or they were not investigated closely. More detailed study of the reaction of diazomethane with the isopropylnitroamine suggested the formation of a secondary nitroamine and the isomeric *O*-ester in the ratio 7 : 3.[48,53]

The reaction with diazomethane is usually carried out in non-polar solvents; we think that it can be described by the scheme:



After the release of nitrogen from the intermediate "diazonium" cation the nitroaminium ion can complete the octet of the carbon atom either by the electron pair of the amine nitrogen (when the nitroamine-nitrogen is not solvated), or owing to the electron pair of the oxygen of the nitro-group (when there is partial polarisation of the nitroammonium anion), which also leads to the products of *N*- and *O*-alkylation, or to their mixtures.

Alkylation by alkyl halides and dimethyl sulphate. The alkylation of the salts of nitroamines with alkyl halides has been studied in greater detail than the alkylation of primary nitroamines with diazoalkanes. The direction of the reaction here depends significantly on the nature of the cation. The silver salts of nitroamines usually form *O*-alkylacylnitroamines[30]:



Whereas sodium or potassium salts form *N*-alkylation products preferentially[24,27,182]. Thus the sodium salt of isopropylnitroamine with methyl iodide gives 60% isopropylmethylnitroamine and 9% *N*-isopropyl-*O*-methyl acinitroamine; the silver salt of the same nitroamine forms a mixture of the secondary nitroamine and its *O*-isomer in the ratio 1 : 10. On the basis of the sodium salts isopropyl-, butyl-, and octyl-nitroamines with the corresponding alkyl iodides, di-isopropylnitroamines, dibutylnitroamines, and dioctylnitroamines were obtained in yields of 14, 12, and 32%; the yields of the *O*-isomers were respectively 26, 24, and 30%. It was noted that the sodium salt of cyclohexylnitroamine is not alkylated by cyclohexyl iodide[56].

In the primary dinitroamine series the alkylation of the monopotassium salt of ethylenebisnitroamine with methyl iodide and dimethyl sulphate was studied. In both instances *N*-methyl-*NN'*-dinitroethylenediamine is isolated. In the alkylation of the dipotassium salt of ethylenebisnitroamine with dimethyl sulphate, *NN'*-dinitro-*NN'*-dimethylethylenediamine is formed[38]. The potassium salt of isopropylnitroamine gives equal proportions of the *N*- and *O*-isomers with dimethyl sulphate[183].

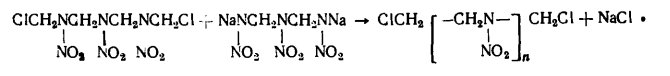
Hence the alkylation of salts of nitroamines with alkyl iodides or dimethyl sulphate often cannot serve as a convenient method for obtaining the secondary nitroamines, but it is completely suitable for the synthesis of *O*-alkylacinitroamines, which are studied as models of the aci-form of the nitroamines[54].

An interesting and practically useful series of papers deals with the alkylation of salts of nitroamines by chloroderivatives containing an active chlorine atom. Picryl chloride and the potassium salt of methyl nitroamine form tetryl in good yield[32]. Ethyl-, propyl-, and butyl-picrylnitroamines can be obtained similarly[26]. *N*-(Chloromethyl)nitroamines and *N*-(nitroxymethyl(-nitroamines react with the sodium salts of nitroamines, the yields of the resulting alkylation products varying from 15 to 81%[184]:

In this reaction a series of $\alpha\omega$-dimethylpolymethylenenitroamines

$$RN(NO_2)[CH_2N(NO_2)]_nR;$$

is obtained; 2,4,7,9-tetranitro-2,4,7,9-tetra-azadecane, and nitroaminoalkyl derivatives of nitrourethane[184]. In the condensation of the disodium salts of dinitroamines with bis-*N*-(chloromethyl)nitroamines polymeric compounds with nitroaza-groupings in a chain are formed[185]:



Acylation of primary nitroamines. Until recently it was thought that acid anhydrides do not attack primary nitroamines[21,24,43]. However, recently Woodcock[75] succeeded in obtaining ethylenebisnitroacetamide in small yields by the action of acetic anhydride on ethylenebisnitroamine.

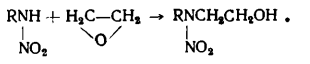
In studies at the end of the last century it was shown that the acid chlorides of organic acids either do not react with primary nitroamines or bring about complete decomposition. Acetyl chloride reacts with the silver salts of methylnitroamine and propylnitroamine with release of dinitrogen oxide[21]. Benzoyl chloride acts similarly on methyl- and isopropyl-nitroamines.

It was found recently that the potassium and silver salts of the esters of *N*-nitroglycine and *N*-nitroalanine are exceptions. They are smoothly acylated at the nitrogen by acetyl chloride, benzoyl chloride, and 3,5-dinitrobenzoyl chloride[115]. The formation of *O*-acylation products is almost not observed.

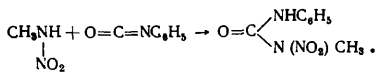
There have been reports of the reasons for such an unusual course of reaction in the failure of Kornblum's rule[186,187] for the alkylation of mesomeric anions. Starting from the fact that the alkali salts of nitroamines react with acylating agents at different rates, and silver salts do not react without catalytic additions of pyridine the investigators suggest that the salts have a chelate, not an ionic, structure. Sodium and potassium salts exist in solution in the form of associates in which the oxygen of the nitro-group is coordinated with metal ions. The silver salts are evidently chelates, therefore acylation is hindered both at nitrogen and at oxygen. The catalytic action of pyridine leads to the breakdown of the complex owing to the formation of a new donor–acceptor bond between the silver ion and the nitrogen atom of the pyridine, as a result of which the nitroamine group is capable of *N*- and *O*-acylation. This point of view satisfactorily explains the effect of the cation in the alkylation of various salts of nitroamines[115].

8. Other Reactions

Primary nitroamines are condensed with ethylene oxide to form the corresponding nitroaminoalcohols[188]:

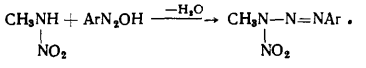


The reaction of methylnitroamine with phenyl isocyanate, leading to the formation of *N*-phenyl-*N'*-nitro-*N'*-methylurea has been described[45]:

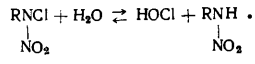


In the action of potassium isocyanate on methylnitroamine free isocyanic acid is released; the formation of the corresponding urea does not take place[45].

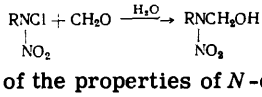
Methylnitroamine reacts with aromatic diazo-compounds. The reaction products in this instance are methylaryl-*N*-nitrotriazenes[189]:



Reference must be made to the production and the study of the properties of the little known *N*-halogeno-*N*-nitroamines. Franchimont and Klobbie[16] did not isolate any individual products from the reaction mixture in the bromination of salts of alkyl nitroamines. Much later Smart and Wright[56], in studying the conversion of alkyldichloroamines to nitroamines expressed the opinion that in aqueous solution there is the equilibrium involving *N*-chloro-*N*-nitroamines:

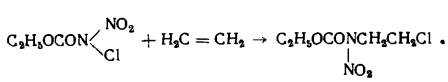


It was recently observed that the chlorine in *N*-chloro-*N*-nitroamines is smoothly converted into the hydroxymethyl group under the action of formaldehyde[190]:

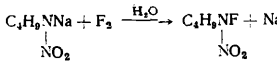


Detailed study of the properties of *N*-chloro-*N*-nitroamines has not been studied in detail nor has the chlorination of primary nitroamines been investigated. However, *N*-chloro-*N*-nitroamines should exhibit extremely interesting chemical properties owing to the strong polarisation of the chlorine atom under the influence of the nitroamino-group, which should lead, in turn, to great lability of the chlorine in reactions with nucleophilic compounds.

In this connection it is interesting to note that primary aromatic nitroamines are readily chlorinated by hypochlorous acid to the unstable *N*-chloro-*N*-nitroamines[191,192]. The production of *N*-chloro-*N*nitrourethane by the action of sodium hypochlorite on a solution of nitrourethane in sulphuric acid and its addition to ethylene and cyclohexene[193]:

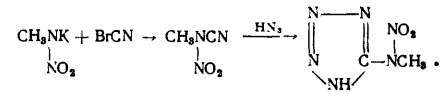


Elemental fluorine reacts readily with salts of nitroamines in an aqueous medium with the formation of *N*-fluoro-*N*-nitroamines. This reaction takes place, for example, with the isomeric butylnitroamines[194]. A thermochemical investigation of the compounds synthesised was also made[195,196].



N-Fluoro-*N*-nitroamines are low-boiling unstable liquids. *N*-Bromo- and *N*-iodonitroamines are unknown.

The reaction of the potassium salt of methylnitroamine with cyanogen bromide, taking place with the formation of *N*-cyanomethylnitroamine has also been described. Without isolating the latter in the pure state it was converted into 5-methyl-5-nitroaminotetrazole by treatment with hydrogen azide[197]:

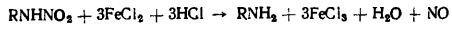


Methylnitroamine reacts vigorously with methylmagnesium iodide[1] with liberation of gaseous products. The products were not identified.

V. ANALYTICAL DETERMINATION

Four qualitative reactions for nitroamines are known: (1) the Franchimont reaction[23]; (2) Thiele and Lachman's reaction[87]; (3) Bamberger's reaction[198]; and (4) Lieberman's reaction[199]. All these reactions are discussed in sufficient detail in Houben–Weyl's monograph[200].

Quantitative methods of analysis of nitroamines for dinitrogen oxygen liberated in the decomposition of nitroamines by hydrochloric acid and iron(II) chloride and also in a Lunge nitrometer[201]:



If the physicochemical methods of identification of primary nitroamines were developed rather intensively in recent years (see Section III), the chemical methods were perfected very poorly and there have been no significant approaches in this field recently. Mention must only be made of the method of identification of primary nitroamines in the form of *S*-benzylthiuronium salts[55]. The latter are formed in good yields on mixing aqueous solutions of *S*-benzylthiuronium hydrochloride with the sodium salts of primary nitroamines. The *S*-benzylthiuronium salts of the primary nitroamines crystallise well from 50% ethanol and have precise melting points. Thus the *S*-benzylthiuronium salt of methylnitroamine melts at 117°C, that of ethylenebisnitroamine at 125–129°C, and that of benzylnitroamine at 127°C.[55]

VI. CERTAIN ASPECTS OF PRACTICAL USE

Judging by the published information, some of the primary aliphatic nitroamines have definite practical value as explosives. The most important of these is ethylenebisnitroamine, which was manufactured in the U. S. A. on an industrial scale under the commercial name of "Haleite"[101]. Ethylenebisnitroamine was used as a high explosive[4]; it can also be used as a component of missile explosives[5] and as a main or reduced charge in percussion cap–detonators instead of tetryl[5].

Methylnitroamine is a low-melting explosive, more powerful than tetryl but weaker than hexogen[12]. It is recommended for use in explosive compositions mixed with T. E. N.[6]

Nitroaminoethanol nitrate and 1-nitroamino-2-nitroxypropane have been suggested as plasticisers for cellulose nitrate.

In recent years there have been patents on the possibility of using primary nitroamines in rocket technology.

Patents have been granted on the use of nitroamide and several primary alkylnitroamines as monopropellents [123,141]. Ethylenebisnitroamine and its hydrazinium salts are recommended as components of mixed rocket propellents [7,202]. The nitroaza-polymer

$$ClCH_2\left[N(NO_2)CH_2\right]_n CH_2Cl$$

obtained by condensation of a salt of a dinitroamine with a bis-*N*-(chloromethyl)-*N*-nitroamine has been recommended as a binder in solid rocket propellents [185].

Nitroamines have interesting and important prospects for use for other purposes. For example, a patent has been granted for the use of aliphatic nitroamines as weed-killers [203] and as effective plant growth stimulators [8,204,205]. Some of the nitroamines are recommended as additives for diesel fuel to increase the octane number [198], for removing the deposit in internal combustion engines [10], and also special additions in dyeing. [11]

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Zelinskii Institute of
Organic Chemistry,
Academy of Sciences of
the USSR, Moscow

U. D. C. 547.442/443

Bis-(β-diketones)

E.S.Krongauz and A.M.Berlin

Methods of synthesis of various types (including those containing the ferrocene structure) of bis-(β-diketones) which are of interest as intermediates in organic synthesis, owing to their high reactivity, are described. The physical and chemical properties of these tetraketones, due to their structural features, to the presence of four carbonyl groups in the molecule, and to ketol-enol tautomerism are examined. 119 references.

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I. INTRODUCTION

Tetraketones, like other carbonyl compounds, exhibit high reactivity and can therefore serve as intermediates for the synthesis of aliphatic, aromatic, heterocyclic, and high-molecular-weight compounds.

The interest in tetraketones arose in recent years when existing methods for their preparation were perfected and new methods developed. The greatest number of papers relates to the use of tetraketones for the synthesis of new compounds, especially those of the heterocyclic series, which have attracted the attention of both chemists and of investigators in the sciences bordering on chemistry. Tetraketones have been used successfully for the synthesis of a new class of thermally stable polymers containing macromolecules of heterocycles in chains: polypyrazoles, polyquinoxalines, polyquinolines, and also for the obtaining coordination polymers with various metals.

Polycoordination and polyheterocyclisation are comparatively new reactions in macromolecular chemistry and their subsequent development should also extend the regions of use of tetrafunctional compounds, including tetraketones.

The present review considers the most abundant representatives of tetraketones—bis-(β-diketones) of various structures: linear, of the type

$$RCOCH_2CO-Y-COCH_2COR$$

and branched, of the types

$$[(RCO)(R'CO)CH]_2CHR'' \text{ and } (RCO)(R'CO)CH-Y-CH(RCO)(R'CO).$$

Other tetracarbonyl compounds are not considered here, since they have been studied less and are little used.

The review covers the periodical literature on these tetraketones up to 1st January 1968.

II. SYNTHESIS OF BIS-(β-DIKETONES)

1. The $RCOCH_2CO-Y-COCH_2COR$ Type

a. The Claisen condensation. Bis-(β-diketones) of the general formula

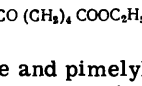
$$RCOCH_2CO-Y-COCH_2COR\ ,$$

can be obtained by two main methods: the Claisen condensation and direct acetoacetylation of aromatic compounds. The most prevalent method is the Claisen condensation, which consists in the treatment of a dicarbonyl compound, usually an ester of a dicarboxylic acid ($R'OOC-Y-COOR'$) with a ketone ($RCOCH_3$) or ethyl acetate in the presence of sodium or potassium amide[1-13]. For example[1]:

$$CH_3OOC-Y-COOCH_3 + 2C_6H_5COCH_3 \rightarrow C_6H_5COCH_2CO-Y-COCH_2COC_6H_5 + 2CH_3OH.$$

Despite its universality this method has several limitations: the Claisen condensation is accompanied by side-processes, which considerably reduce the yield of the final bis-(β-diketone), make it more difficult to isolate in a pure form, and sometimes make the synthesis completely impossible. For example, the Claisen condensation cannot be used for making adipylbisacetophenone and pimelylbisacetophenone ($Y = [CH_2]_4$ and $[CH_2]_5$; $R = C_6H_5$), because under these conditions the Dieckmann reaction takes place more readily, leading to the formation, in the first example, of 2-ethoxycarbonylcyclopentanone in 77% yield[1]:

$$C_6H_5COCH_3 + C_2H_5OCO(CH_2)_4COOC_2H_5 \rightarrow$$



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Adipylbisacetophenone and pimelylbisacetophenone were obtained by treatment of a suspension of the sodium salt of the ketone in ether with the dichloride of the corresponding

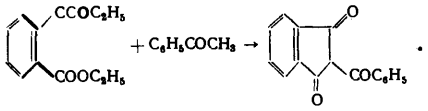
acid[1]. This method was used earlier for the synthesis of certain β-diketones[14-17]. It was then noted that the use of three equivalents of the sodium salt of the ketone per one equivalent of the acid chloride ruled out any possibility of further acylation.

The Claisen condensation also has other limitations: esters of malonic and succinic acids usually undergo an aldol condensation and a Stobbe condensation respectively. For example, with diethyl succinate the condensation with acetophenone leads to the formation of an ester of an unsaturated acid in 92% yield:

$$C_6H_5COCH_3 + C_2H_5OOC(CH_2)_2COOC_2H_5 \xrightarrow{NaH} \rightarrow C_6H_5C(CH_3)=C(COOC_2H_5)CH_2COOC_2H_5.$$

It is interesting to note that in the condensation of di-t-butyl succinate with acetophenone in the presence of NaH succinylbisacetophenone was obtained in 19–34% yield in addition to the half-ester (yield 56–64%).[9]

Several bis-(β-diketones) cannot be obtained by the Claisen condensation owing to the occurrence of intermolecular cyclisation. For example, 2-benzoyl-1,3-diketoindane was obtained in the reaction of diethyl phthalate and acetophenone in the presence of sodium ethoxide[18]:

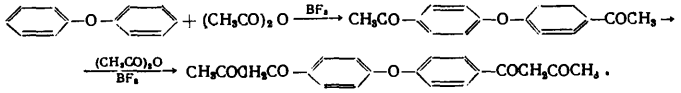


The reactions with acetone and ethyl methyl ketone take place in a similar fashion.

The mechanism of the Claisen condensation in the synthesis of bis-(β-diketones) is analogous to the mechanism of the acylation of ketones by esters. The acylation probably takes place by a three-stage mechanism, as for the formation of acetoacetic ester[15].

b. Direct acetoacetylation. This method is suitable for the synthesis of only aromatic bis-(β-diketones) in which R = CH_3, and Y = an aryl biradical of various structures. The method consists in the direct acetoacetylation of aromatic compounds with two benzene rings by an excess of acetic anhydride in the presence of BF_3.[19,20]

In comparison with the Claisen condensation this method does not require the use of solvents and metallic sodium (or sodium amide), is simple and convenient to use, and gives higher yields and purer bis-(β-diketones). With diphenyl oxide as an example the reaction can be represented by the following overall equation:

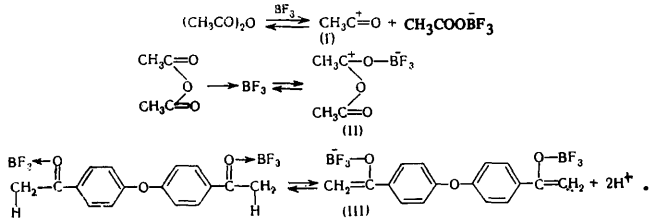


The first stage of the reaction is evidently the formation of diacetyl compounds by a Friedel-Crafts reaction.

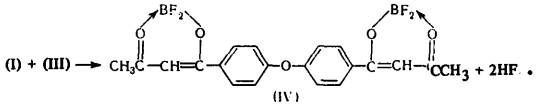
The formation of bis-(β-diketones) from diketones can occur either as a result of their direct *C*-acylation or by the *O*-acylation of the diketone with subsequent *C*-acylation of the resulting ester of the enol form of the diketone[21].

The large consumption of boron trifluoride is probably due to the *C*-acylation of the diketone being connected with the conversion of both the acid anhydride and also the diketone into reactive intermediate compounds, which then participate further in the condensation.

The mechanism of this reaction has not been investigated. Presumably, as for the synthesis of β-diketones[22] the acid anhydride forms a carbonium ion—of type (I) or (II)—and the diketone a complex of the enol type, which by analogy with ordinary enols should correspond to structure (III):



Condensation of the carbonium ion (I) with the enol complex (III) leads to the formation of a complex of the tetraketone (IV):



The *O*-acetylation of a diketone evidently leads to the proton-catalysed enolisation of the diketone accompanied by the acylation of the enol formed. Subsequently *C*-acylation of the ester of the enol form of a diketone by carbonium ions (I) or (II) lead to the formation of an ester of the enol form of a bis-(β-diketone), which after removal of the acid fluoride also forms the complex (IV).[20-22]

In the initial period of the reaction when there is still little acid in the reaction mixture, a bis-(β-diketone) can be formed only by *C*-acylation of a diketone. However, with the accumulation of acid in the reaction mixture formation of a bis-(β-diketone) can also take place indirectly and in the last period of the reaction this second path can become dominant. Since the acid which is formed as a side-product of the reaction catalyses not only the *O*-acetylation of ketones but also their self-condensation (aldol type) the best yields of bis-(β-diketones) were obtained when the rate of introduction of BF_3 into the reaction was maximal[20].

The direct acetoacetylation of diphenyl oxide, diphenylmethane, diphenylethane, diphenyl disulphide, and diphenyl esters of ethylene glycol and diethylene glycol by acetic anhydride in the presence of BF_3 gave the corresponding bis-(β-diketones), the structure of which was confirmed by a counter-synthesis by the Claisen condensation[20].

2. Bis-(β-diketones) of the $[(RCO)(R'CO)CH]_2CHR''$ Type

Bis-(β-diketones) of this type are obtained by the reaction of β-diketones with aldehydes in the presence of the appropriate catalyst[23-39].

The synthesis of bis-(β-diketones) of the $[(RCO)(R'CO)CH]_2CHR''$ type, evidently proceeds through the formation of an intermediate product of the $(RCO)(R'CO)CH{=}CHR''$ type, which adds a second molecule of the β-diketone by a Michael reaction, for example, in the formation of 2-phenyl-1,1,3,3-tetra-acetylpropane during the reaction of equimolecular amounts of benzaldehyde and acetylacetone[23]. In a series of instances, for example, in the reaction of acetylacetone with cinnamaldehyde[24], 2-hydroxynaphthaldehyde[25], or salicylaldehyde[26], the formation of an unsaturated β-diketone $(CH_3CO)_2C{=}CHR''$ was not observed.

Bis-(β-diketones) with a trifluoroacetyl group could not be obtained by this method, evidently because of their hydrolytic cleavage, analogous to that of the simple β-diketones containing a trifluoroacetyl group[26-28].

3. Bis-(β-diketones) of the (RCO)(R'CO)CH–Y–CH(RCO)(R'CO) Type

Bis-(β-diketones) in which R=R'=CH_3 and Y is a single bond are obtained by the reaction of a sodium salt of a β-diketone with iodine in ether and ethanol[40-42].

For the synthesis of bis-(β-diketones) with R=R'=CH_3, Y = $[CH_2]_2$, $[CH_2]_6$, $[CH_2]_{10}$, and 1,4-$(CH_2)_2C_6H_4$ a method suitable for the synthesis of monoalkylated β-diketones RCOCHR"COR' was used, consisting in the alkylation of a β-diketone (sodium salt of acetylacetone) with a dihalogenoalkane[43-48,56,57]. The reaction is usually carried out in a sealed ampoule[46-49] or in a high-boiling solvent[50]. The dihalogenoalkane can act as the solvent, which allows the reaction to be carried out at higher temperatures. However, the presence of a large excess of the dihalide is unfavourable for the reaction since it assists intramolecular condensation.

It was found that the best alkylation conditions are the reaction of acetylacetone (3 moles) with the dihalogenoalkane (1 mole) in a medium of t-butyl alcohol in the presence of sodium t-butoxide (2 moles) under reflux with vigorous stirring[40]. 4,4'-Bis-(2,2-diacetoethyl)biphenyl and 4,4'-bis-(2,2-diacetoethyl)diphenyl oxide were obtained by boiling 4,4'-bis(bromomethyl)biphenyl and 4,4'-bis(bromomethyl)diphenyl oxide with sodium acetylacetonate in acetylacetone[51].

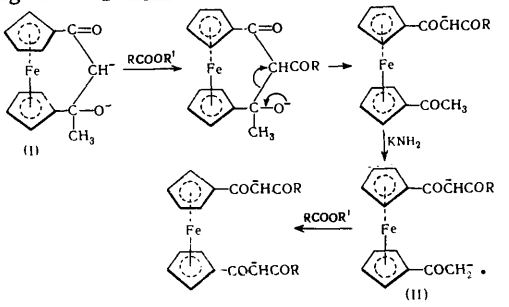
It should be noted that the alkylation of sodium acetylacetonate by dihalogenoalkanes in the synthesis of bis-(β-diketones) takes place exclusively at the carbon atom. Evidently for bis-(β-diketones) a type S_N2 transition state is established preferentially, in which the alkylation is directed towards the less electronegative atom, here carbon.

The observed direction of alkylation agrees with the views of Nesmeyanov and Kabachnik concerning the increasing tendency to reaction with transfer of the reaction centre (from oxygen to carbon) with increase in the ionic character of the bond of an ambidentate anion with a metal. Moreover, in addition to polar factors steric effects have a great effect on the direction of alkylation[52-54].

Neuse and Crossland[57] recently described some ferrocene-containing bis-(β-diketones) having a linear structure of the $RCOCH_2CO–Y–COCH_2COR$ type, where Y = ferrocene.

1,1'-Bis(acetylaceto)ferrocene and 1,1'-bis(benzoylaceto)ferrocene were obtained by a Claisen condensation from 1,1-diacetylferrocene by the method of Hauser and coworkers[16]; 1,1'-bis(formylaceto)ferrocene was synthesised by a modified Schlögl method[17], which included condensation of 1,1'-diacetylferrocene with ethyl formate.

A mechanism has been proposed for the acylation of diacetylferrocene in the presence of potassium amide, which takes place through the formation of the intermediate cyclic carbanion (I) and dianion of the bis-(β-diketone) (II), according to the scheme:



The authors note that the introduction of the second acyl group is easier than the first which can be explained by the better solubility of the dipotassium salt of the dicarbanion (II) compared with the dipotassium salt of the dianion (I), and possibly also the isomerisation of cis-dianion (II) into the trans-configuration as a result of the repulsion of the negative charges of the two side chains[57].

III. PHYSICAL PROPERTIES AND STRUCTURE OF THE BIS-(β-DIKETONES). KETO–ENOL TAUTOMERISM

Most of the bis-(β-diketones) described above are crystalline substances with rather high melting points. The overwhelming majority of the bis-(β-diketones) give a specific cherry-red colour with a methanol solution of $FeCl_3$.

A characteristic feature of the bis-(β-diketones) is the keto–enol tautomerism which has been studied in detail by the example of dicarbonyl compounds[58]. In recent years a significant contribution to the development of a quantitative theory of keto–enol equilibrium by the example of β-diketones has been made by Kabachnik and coworkers[59-62].

Since linear bis-(β-diketones) of the type $RCOCH_2CO–Y–COCH_2COR$ can be regarded as derivatives of benzoyl acetone and branched bis-(β-diketones) of the $[(RCO)_2CH]_2Y$ and $[(RCO)(R'CO)CH]_2CHR'''$ types as 3-substituted acetylacetone. They will possess to a considerable extent the keto–enol equilibrium found for β-dicarbonyl compounds. However, there are some specific features in the keto–enol tautomerism of bis-(β-diketones), owing to the peculiarities of their structure.

As an investigation of their infrared and ultraviolet spectra showed, bis-(β-diketones) of the $RCOCH_2CO–Y–COCH_2COR$ type exist predominantly in the *cis*-enol form in the solid state and in 95% ethanol solution[1]. This is shown by the absence of absorption characteristic for the carbonyl group in the infrared spectra of almost all the bis-(β-diketones) studied (in the range 5.7–5.9 μm), except for oxalyldiacetone and adipyldiacetone. Furthermore, the 16 bis-(β-diketones) studied have either one or two absorption bands of high intensity (in the range 6.2–6.5 μm) ascribable to an enol chelate bond. The absence of hydroxyl absorption in the spectra of ten of the 16 bis-(β-diketones) (2.95 μm region) is evidently due to its displacement and the superposition of the bands of the stretching vibrations of the C–H bonds. A similar effect was observed earlier in the spectra of acetylacetone and other enolised β-diketones, which was explained by the influence of the strong intramolecular hydrogen bonds[22,55,63,64].

The position of the enol-chelate bonds in the infrared spectra is determined by the structural features of the bis-(β-diketones). Thus, the enol-chelate bands in sebacylbisacetone are found at 6.08 and 6.24 μm, and in oxalyldiacetone at 6.25 and 6.33 μm. This displacement is the result of the great degree of conjugation possible in oxalyldiacetone. Replacement of the alkyl terminal groups in the latter by phenyl groups increases the degree of conjugation and correspondingly the oxalyldiacetophenone has an enol–chelate band at 6.25–6.40 μm.[1]

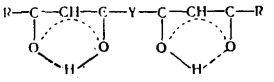
When two β-diketone groups are separated by a methylene chain there is less conjugation. Thus succinyl-, pimelyl-, suberyl-, azeloyl-, and sebacyl-diacetophenone have enol–chelate absorption at 6.20 and 6.34 μm.[1]

The position of the keto–enol equilibrium is significantly affected by the nature of the solvent. It is found that a tendency for bis-(β-diketones) to exist in the keto-form is more pronounced in tetrachloroethylene than in the solid state. As studies of the ultraviolet spectra showed, in

95% ethanol bis-(β-diketones) of this type exist predominantly in the enol form[1]. A displacement of the position of the enol band in the ultraviolet spectra of the bis-(β-diketones) to the side of 310 nm can be qualitatively connected with conjugation, which appears in the presence of terminal phenyl groups and/or phenylene bonds. For example, when R = phenol and Y = a methylene chain, the enol band is noted at ~ 312 nm (succinyldiacetophenone 320 nm, and oxalyldiacetophenone even 333 nm); terephthalyldiacetone has absorption at 340 nm, isophthalyldiacetophenone at 357 nm, and terephthalyldiacetophenone at > 360 nm.

For certain bis-(β-diketones) the enol content has been determined quantitatively from the ratio $\varepsilon_m/\varepsilon_e$ (ε_m is the observable extinction at 310 nm, where the absorption of the keto-form should be insignificant, and ε_e is the extinction of the pure enol), and on the basis of PMR spectra. The calculated concentrations of the enol in 95% ethanol for the following bis-(β-diketones) are: suberyldiacetophenone 77.8%; azelyldiacetophenone 82.8%; sebacyldiacetophenone 88.4%; and 4,4′-bis(acetoacetyl)diphenyl oxide 100%.[1,65]

On the basis of the results of spectroscopic investigations and also the inertness of bis-(β-diketones) of the $RCOCH_2CO-Y-COCH_2COR$ type in certain reactions in which the ketonic form is absent, the following structure was attributed to them:



Evidently, as a result of the enolisation of the bis-(β-diketones) a claw-shaped complex (chelate) is formed and the fractional negative charge arising on the carbon is delocalised between the carbon and carbonyl-oxygen atoms, which leads to the stabilisation of the molecule and a decrease in its reactivity[19].

It should also be noted that the keto-enol equilibrium in the bis-(β-diketones) is extremely stable. Unlike the usual mobile keto-enol equilibrium known in acetylacetone, acetoacetic ester, and other β-diketones, the principal enol form is retained and reacts even in solutions of these bis-(β-diketones).

Bis-(β-diketones) of the $[(RCO)(R'CO)CH]_2CHR''$ type (the so-called branched tetraketones) exist predominantly in the keto-form in the solid state according to the infrared spectra. This is shown by the intense carbonyl absorption at 5.77–5.85 μm and the weak absorption in the 6.25 μm range, characteristic of enol–keto absorption. In the infrared spectra of the bis-(β-diketones) of this type there are maxima at ~ 2.95 μm, corresponding to the vibrations of the strained hydroxyl bonds. In nine examples it was found that the hydroxyl bonds can be shifted, bringing about displacements of the vibrations of the CH-bonds analogous to the displacement observed in the spectrum of acetylacetone and other enolised β-diketones, and also bis-(β-diketones), which form strong intramolecular hydrogen bonds[63,64].

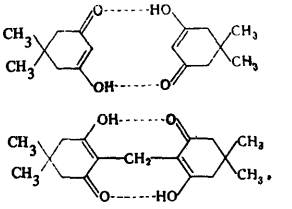
The structure of R and R′ has a considerable influence on the position of the normal carbonyl bond in these bis-(β-diketones). In 11 compounds in which R = R′ + CH_3 five have two carbonyl maxima at 5.78 and 5.85 μm, and six of the compounds have only one intense maximum at ~ 5.85 μm. The compounds

$[(CH_3CO)(C_6H_5CO)CH]_2CHC_6H_5$ and $[(C_6H_5CO)_2CH]_2CH_2$

have two carbonyl group absorption maxima in the ranges 5.83 and 5.94 μm and 5.91 and 5.97 μm, respectively. These changes in the position of the carbonyl bonds are evidently due to an increase in the carbonyl conjugation.

The enol-chelate absorption of these compounds is very weak. Only in three compounds of the $[(CH_3CO)_2CH]_2CHR''$ type, where R″ = 2-ClC_6H_4, 2-CH_3O-C_6H_4, or 2-C_5H_4N, is the intensity of the enol-chelate absorption and carbonyl absorption comparable. The reason for this is not clear. Possibly here there is the effect at all the R″ of these three compounds of heteratoms or substituting groups in the *ortho*-position, which creates steric and/or polar effects favourable for an enol-chelate structure.

In the infrared spectra of solid methylenebis(dimedone) there are present the vibrations of weak intensity of conjugated carbonyl at 5.90 μm and of enol-chelate bonds of high intensity at 6.10 and 6.30 μm. This picture is completely analogous to the dimedone spectrum, which suggested an analogy in their structure: an enol-chelate structure resulting from dimerisation has been proposed for dimedone and an intramolecular enol-chelate structure for methylenebis(dimedone)[63]:



Methylenebis(dimedone) does not form the cherry-red colour characteristic of bis-(β-diketones) with a methanol solution of $FeCl_3$.

An investigation of the ultraviolet spectra of bis-(β-diketones) of the $[(RCO)(R'CO)CH]_2CHR''$ type in 95% ethanol showed the dependence of the extinction coefficient on concentration; in some instances the extinction coefficient increases with increase in concentration—for example, for the compound

3,4-$(CH_3O)_2C_6H_3CH[CH(COCH_3)_2]_2$

—in other instances it decreases as the concentration is raised—for example,

$[(CH_3CO)_2CH]_2CHC_5H_4N$,

—in a third group it is independent of concentration—methylenebis(dimedone) and certain other compounds[40].

Such anomalies, which are explicable for acyclic β-diketones by their low acidity and inability to form enol-chelates[68] unsuitable for finding differences in the spectra of bis-(β-diketones) since they are all capable of forming enol-chelate structures. The differences in the extinction coefficients can be best explained by a change in the conjugation of the enol with change in concentration[67].

A comparison of the ultraviolet spectra of the β-diketones and the related bis-(β-diketones) of the $[(RCO)(R'CO)CH]_2CHY$ type that the latter have much less tendency to enolisation, with the structure and spectroscopic characteristics of the bis-(β-diketones) determined by the nature of R, R′, and the –Y bonds. Thus benzoyldiacetone in 95% ethanol has mixed keto–enol absorption in the 245.5 nm range ($\lg\varepsilon_m = 3.78$) and the pure absorption of the enol form at 310 nm ($\lg\varepsilon_m = 4.14$).[68] The bis-(β-diketone)

$[(CH_3CO)(C_6H_5CO)CH]_2CHC_6H_5$

has only one intense maximum, at 248.5 nm ($\lg\varepsilon_m = 4.30$), which shows the absence of an enol form. Dibenzoylmethane exists in ethanol almost exclusively in the enol form

($\lg \varepsilon_m = 4.36$ at 345 nm and $\lg \varepsilon_m = 3.92$ at 250 nm); tetra-acetylpropane, on the other hand, has intense absorption at 249 nm ($\lg \varepsilon_m \simeq 4.6$) and weak absorption at 340 nm ($\lg \varepsilon_m = 3.0-3.4$).

Hence unlike the $RCOCH_2CO-Y-COCH_2COR$ type of bis-(β-diketones), which exist in the solid state predominantly in the enol form, the bis-(β-diketones) of the $[(RCO)(R'CO)CH]_2CHR''$ type (where $R'' \neq H$) have a much less expressed tendency to enolisation in the solid state.

Bis-(β-diketones) of the $[(RCO)(R'CO)CH]_2Y$ type show great differences amongst themselves in physical properties and structure. Tetrabenzoylethane is hardly enolised at all (there is no absorption at 340 nm, an intense absorption at 247.5 nm, $\lg \varepsilon_m = 4.89$); tetra-acetylethane, on the other hand, has an intense enol-chelate absorption at 6.27 μm but no carbonyl absorption in the 5.85 μm range. Tetra-acetylpropane has maximum absorption of approximately the same intensity both in the range of vibrations of the ketonic groups and in the enol-chelate region.

In an investigation of the PMR spectra of 1,1,2,2-tetra-acetylethane, 1,1,3,3-tetra-acetylpropane and 1,4-bis-(2',2'-diacetoethyl)benzene a signal for a hydroxyl proton of *cis*-enol form was observed. The chemical shifts of the protons of the OH group measured on the δ scale were 16.85, 15.80, and 16.90 respectively. Our calculations showed that the first is 100% *cis*-enol, the second contains 50% *cis*-enol and 50% ketonic form, and the third 20% *cis*-enol and 80% ketonic form. The PMR results are in complete agreement with the results obtained in studying the infrared spectra of these bis-(β-diketones), and also with their reactivity.

For all three types of bis-(β-diketones) the dissociation constants in water–dioxan mixtures with 75 or 50 vol.% dioxan at 30°C were determined using tetramethylammonium hydroxide as a base[69-71].

It was found that linear bis-(β-diketones) of the $[RCOCH_2CO]_2Y$ type are evidently stronger acids than branched ketones of the $[(RCO)(R'CO)CH]_2CHR''$ and $[(RCO)(R'CO)CH]_2Y$ types, as is shown primarily by the fact that the dissociation constants of branched bis-(β-diketones) were so low that they could not be determined in 75% dioxan.

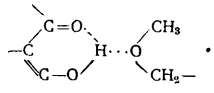
The lower acidity of the branched bis-(β-diketones) is probably connected with the fact that both the β-diketone functions are displaced from the active methylene position. An analogous picture is observed with simple β-diketones: the pK_D of acetylacetone (10.35) in 50% dioxan is less than the pK_D of butylpentane-2,4-dione (12.07).[69]

In general the relative acidity of linear and branched bis-(β-diketones) can be linked with their relative tendency to exist in the enol form in the solid state: linear bis-(β-diketones), which exist in the solid state predominantly in the enol form, are weaker acids than the branched bis-(β-diketones), which have less tendency to enolisation.

In the $C_6H_5COCH_2CO-[CH_2]_n-COCH_2COC_6H_5$ series (n = 4–8) it is interesting to note the peculiar dependence of the value of pK_{D_1} (but not pK_{D_2}) on the chain length *n*. Thus the dissociation of the first proton takes place more slowly for pimelyl ($n = 5$) than for adipyl ($n = 4$), suberyl ($n = 6$) or sebacyl-diacetophenone ($n = 8$) and even more slowly for azelayldiacetophenone ($n = 7$). The difference between the values of pK_{D_1} and pK_{D_2} increases linearly with increase in the chain length from 4 to 8. We were unable to determine pK_{D_2} for azelayldiacetophenone. The fact that the second proton of linear bis-(β-diketones) dissociates with greater difficulty with increase in the chain length, differs from what is to be expected from their behaviour[69].

However, for compounds of the $[(CH_3CO)_2CH]_2[CH_2]_n$ type the second proton dissociates more readily with increase in the chain length: thus the difference between the values of pK_{D_1} and pK_{D_2} equals 4.11 ($n = 0$), 0.49 ($n = 6$), and 0.06 ($n = 10$). The value of pK_D of bis-(β-diketones) of the $[(RCO)(R'CO)CH]_2CHR''$ type is greatly affected by the nature of R, R', and R''. For a given R'' group the derivatives of acetylacetone ($R = R' = CH_3$) have lower pK_D than derivatives of methoxyacetylacetone ($R = CH_3$, $R' = CH_3OCH_2$), although acetylacetone itself has a higher pK_D (10.35) than methoxyacetylacetone (9.66 in 50% dioxan).

To explain this non-correspondence it is suggested that a structure with an intermolecular hydrogen bond between an ethereal oxygen and a chelate hydrogen is formed:



Hence the third oxygen reduces the lability of a proton and increases pK_D itself.

In the bis-(β-diketones) series $[(RCO)(R'CO)CH]_2CHR''$ with $R = R' = CH_3$ the compound with $R'' = 4\text{-}CH_3OC_6H_4$ has a higher value of pK_D than the compound with $R'' = C_6H_5$ (11, 62, and 11.1 respectively), which is attributed to the activating influence of a methoxy-group. An increase in the electronic density at an α carbon atom in relation to the methylene group leads to a decrease in the lability of the proton. The influence of other electron-repelling substituents can be explained similarly[69]. The differences in the structure of bis-(β-ketones) appear not only in the physical properties but also in their behaviour in chemical reactions.

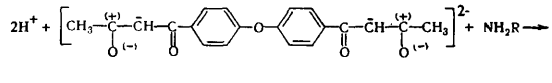
IV. CHEMICAL PROPERTIES OF THE BIS-(β-DIKETONES)

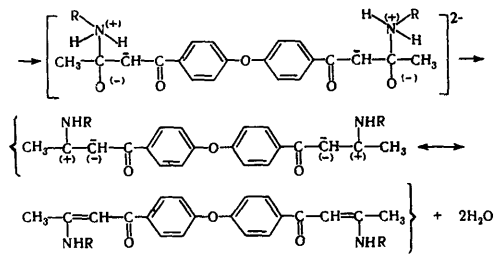
The reactivity of bis-(β-diketones) has been little investigated. As might have been expected from the analogy in structure, the bis-(β-diketones) are greatly reminiscent of β-dicarbonyl compounds. However, there are significant differences in the reactivity of these classes of compounds, which are evidently due to the presence of four carbonyl groups in the molecule of bis-(β-diketones) and of structural features connected primarily with keto-enol tautomerism.

1. Reaction of Bis-(β-diketones) with Amines. Ketoimide–Enamine Tautomerism

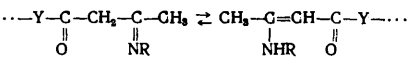
The reaction of linear bis-(β-diketones) of the $RCOCH_2CO-Y-COCH_2COR$ type with some aromatic amines has been studied. Thus 4,4'-bis(acetoacetyl)diphenyl oxide reacts vigorously on heating with aniline, 2-naphthylamine, 4-aminobiphenyl, and other amines, forming the corresponding dianils in high yields[72].

Since the initial 4,4'-bis(acetoacetyl)diphenyl oxide exists predominantly in the enol form, this reaction evidently proceeds owing to polarisation of the bonds of the principal form of the enol, which adds on the amine with subsequent loss of water from the addition product and stabilisation by conjugation:

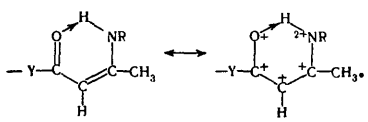




Like the initial 4,4′-bis(acetoacetyl)diphenyl oxide the product of its reaction with an amine can exist in two tautomeric forms, enamine and ketimide:

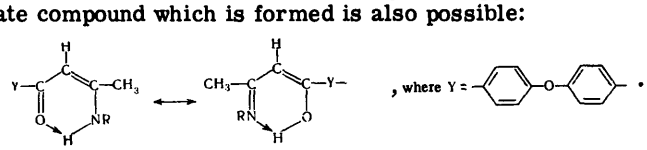


And, finally, the enamine form, like the enol form of the bis-(β-diketone), forms a pseudoaromatic chelate compound:



The "aromatisation" of the enamine-chelate form with the formation of an aromatic system of 6π-electrons should proceed more readily here than in ordinary enols, since the p-electrons of nitrogen are less firmly held than those of oxygen in the enols.

The existence of intramolecular prototropy in the chelate compound which is formed is also possible:

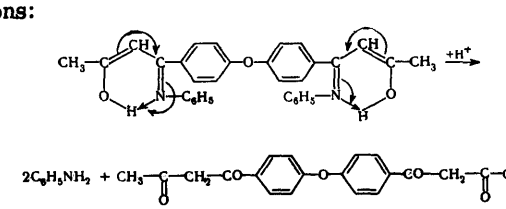


A noteworthy feature, which is characteristic for bis-(β-diketones) and probably for their derivatives, is the complete displacement of the tautomeric equilibrium in solutions, in the solid state, and in melts to the side of one of the possible tautomeric forms.

2. Kolbe Synthesis

Unlike the derivatives of aniline and acetylacetone, the products of the reaction of 4,4′-bis(acetoacetyl)diphenyl oxide with amines are cyclised into derivatives of quinoline with much greater difficulty[72].

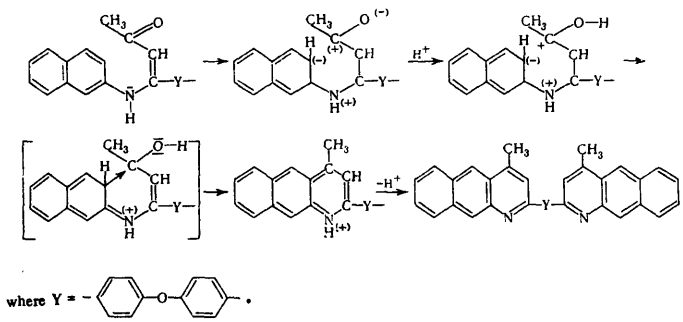
As a result of the reaction the fission of the original dianil into its constituent components is often observed. Evidently, such a direction of reaction can be explained by the fact that displacement of one CH_3 group (acetylacetone) by an aromatic radical (diphenyl oxide residue) leads to the weakening of the nitrogen–carbon bond in the β-arylaminoketone. The presence of an unshared pair of electrons at the nitrogen determines the nucleophilic nature of the NH group and facilitates attack at the side of the hydrogen ions:



The product of the reaction of 4,4′-bis(acetoacetyl)diphenyl oxide with 2-naphthylamine readily undergoes cyclisation under the action of anhydrous HF at 0°C and also on heating with a mixture of 2-naphthylammonium chloride with 2-naphthylamine, forming derivatives of benzoquinoline in ~ 35% yield in both instances. The action of conc. H_2SO_4 brought about hydrammine splitting of the original dianil.

The benzoquinolines obtained by these two methods were not identical in their properties[72]. Evidently under different conditions cyclisation proceeds in different ways.

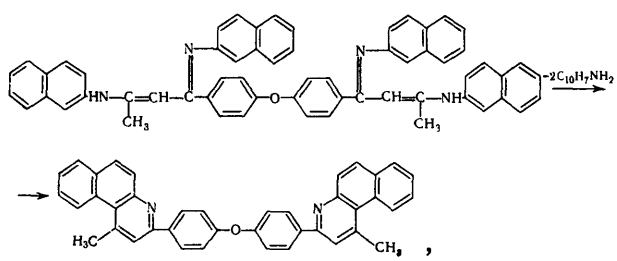
Evidently, under the action of HF a hydroxycarbonium ion is formed which cyclises into an aromatic system when water is lost:



where Y = .

In this system the closure of the naphthalene ring takes place in position 3 and a linear derivative of dibenzo(*g*)quinoline is formed. Its structure is confirmed by the similarity of the ultraviolet spectra of benzoquinoline with the spectra of anthracene, by the characteristic colour of its salts and by fluorescence in ultraviolet light[72].

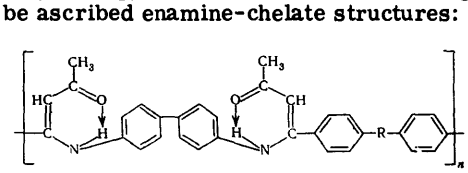
On heating 4,4′-bis(acetoacetyl)diphenyl oxide with 2-naphthylamine in the presence of an equimolecular amount of the amine hydrochloride after Petrov[73], an angular derivative of dibenzo(*f*)quinoline is obtained. Here the reaction evidently proceeds throughout the formation of an intermediate addition compound at the four carbonyl groups:



with subsequent loss of two molecules of 2-naphthylamine.

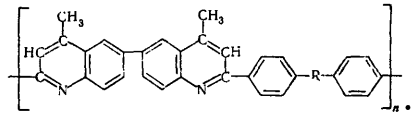
These reactions were extended to aromatic diamines; in particular the reaction of 4,4′-bis(acetoacetyl)diphenyl oxide and 4,4′-bis(acetoacetyl)diphenylethane with benzidine were studied.

Heating a mixture of the initial products leads to the formation of high-molecular-weight polyanils (η_{pr} = 0.6–0.8) which by analogy with the low-molecular-weight products can be ascribed enamine-chelate structures:



where R = –O– or $-[CH_2]_2-$.

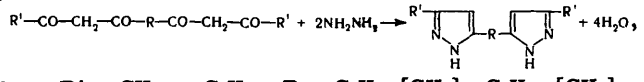
Further heating of the polyanils in a vacuum leads to intramolecular cyclisation and the formation of polyquinolines, with the degree of cyclisation here depending on the temperature and the time of heating in a vacuum[74].



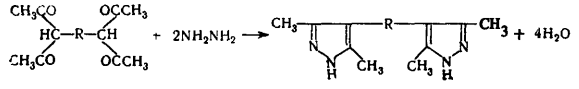
3. Reaction of Bis-(β-diketones) with Hydrazines and Hydrazides of Acids

Bis-(β-diketones) readily undergo condensation, especially with nitrogen-containing compounds (such as hydrazine and its derivatives, hydroxylamine, amidines, urea, etc.), forming addition products at two opposite carbonyl groups of two molecules of the nitrogen-containing compound, with subsequent cyclisation of the addition product and formation of heterocyclic systems: pyrazole, isoxazole, etc. The condensation products, like the original bis-(β-diketones), exhibit tautomerism.

a. Bispyrazoles. 3,5-Bispyrazoles are formed in the reaction of linear and branched bis-(β-diketones) with hydrazine hydrate according to the following scheme[55,75-77]:



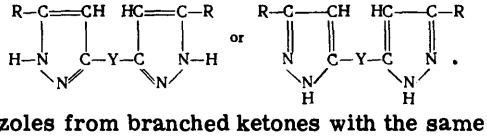
where R′ = CH_3 or C_6H_5; R = C_6H_4–$[CH_2]_2$–C_6H_4, $[CH_2]_3$, C_6H_4–O–C_6H_4, or C_6H_4–S_2–C_6H_4.



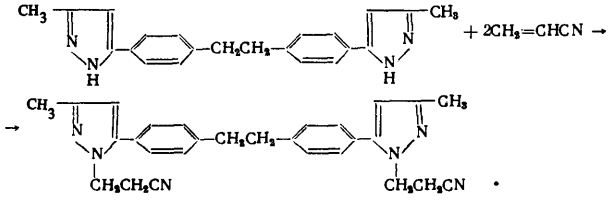
where R = CH_2–C_6H_4–CH_2, $CH_2[C_6H_4]_2CH_2$, or CH_2–C_6H_4–O–C_6H_4–CH_2.

An intermediate product of the reaction is evidently the bishydrazone formed in the reaction of the carbonyl groups of the ketone with the amino-group of the hydrazine, which then closes into a pyrazole ring.

Since the bispyrazoles of linear bis-(β-diketones) have different substituents in positions 3 and 5, two structural isomers are possible:



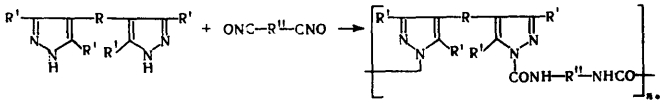
Bispyrazoles from branched ketones with the same substituents do not have isomers, thanks to the symmetry of the molecule. Bispyrazoles, like pyrazoles, form salts with strong bases (for example, hydrochlorides) they are capable of undergoing cyanoethylation, acylation, etc. The cyanoethylation of 4,4′-bis-[3(5)-methylpyrazolyl-5(3)]diphenylethane on heating it with acrylonitrile in an ampoule has been described[75]:



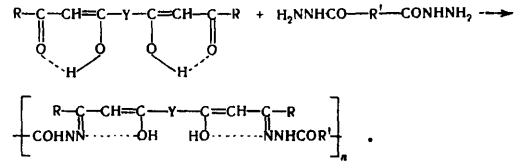
When bispyrazoles react with acetyl chloride, the corresponding *N*-acyl derivatives are formed[75,78-80].

The replacement of the acetyl chloride in this reaction by the acyl chlorides of dicarboxylic acids leads to the formation of polyacylpyrazoles[76].

When di-isocyanates are used instead of the dicarboxylic acid chlorides polymers containing pyrazole rings and amide bonds –CO–NH– in a chain were obtained[87]:



b. Polyacylhydrazones and polyacylpyrazoles of linear bis-(β-diketones). The reaction of linear bis-(β-diketones) with hydrazides of dicarboxylic acids leads to the formation of polyacylhydrazones:

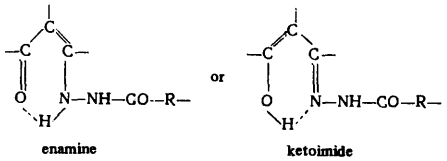


Evidently the formation of polyacylhydrazones takes place analogously to the reactions of monocarbonyl compounds with such reagents as semicarbazide, hydroxylamine, amines, etc., that is, through the addition of the amino-group of the hydrazide at the >C=O bond, with subsequent loss of water. Therefore such reaction will proceed more readily with a ketonic or *trans*-enolic form of a bis-(β-diketone) having a free carbonyl group and with greater difficulty with *cis*-enols in which the carbonyl group is connected by an intramolecular hydrogen bond into a stable six-membered ring.

The polyacylhydrazones which have been formed also have a chelate structure stabilised by an intramolecular hydrogen bond, which is shown by the presence in the ultraviolet spectrum of a polyacylhydrazone of absorption in the range λ_{max} = 335 nm; the band with λ_{max} at 300 nm is ascribed to the presence of a *cis*-enol with a stable hydrogen bond[40].

In the infrared spectrum of polyacylhydrazone as well as an intense absorption band in the 1720 cm^{-1} range attributable to the vibrations of a hydrazide C=O group there is a maximum in the range 1600–1620 cm^{-1} characteristic for a *cis*-enol[75].

The enolisation of polyacylhydrazones can be effected both as a ketomide and as an enamine structure[82]



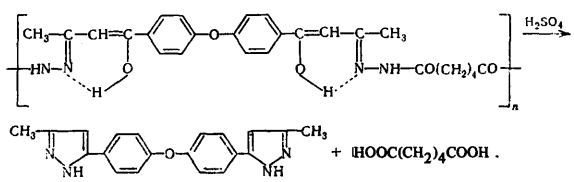
enamine ketoimide

and it is difficult to choose between these. Both these structures are stabilised by intramolecular hydrogen bond, which makes further attack by nitrogen on the carbonyl oxygen more difficult in the formation of a pyrazole ring.

Having investigated the kinetics of the formation of polyacylhydrazones by the example of the reaction of 4,4′-bis-(acetoacetyl)diphenyl oxide with the dihydrazide of adipic

acid in dimethylformamide solution at 90–120° was investigated by ultraviolet spectroscopy. It was shown that under the chosen conditions the process obeys the laws of a first order irreversible reaction. The rate constants and the activation energy of the process (17 kcal mole^{-1}) were determined[83].

The polyacylhydrazones are stable to long boiling in water and also to brief action by conc. H_2SO_4 (5–10 min). After 24 h in a solution in H_2SO_4 at room temperature polyacylhydrazones form the corresponding bispyrazoles and an acid, in quantitative yield:



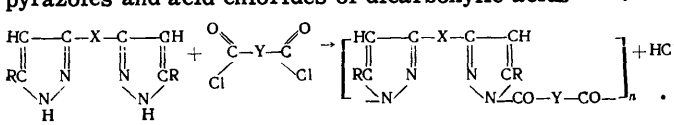
On treating polyacylhydrazones with hot hydrochloric acid the bispyrazolium chloride is formed. Concentrated solutions of alkalis also decompose the polyacylhydrazones.

The structure of the polyacylhydrazones was confirmed by comparing their ultraviolet spectra in H_2SO_4 with the ultraviolet spectrum of a model compound—4,4′-bis(acetoacetyl)diphenylethane acetylhydrazone. The ultraviolet spectrum of the polyhydrazone based on sebacylbisacetophenone in methanol is similar to the spectrum of the model compound in methanol, but has a bathochromic shift of 40 nm.[75]

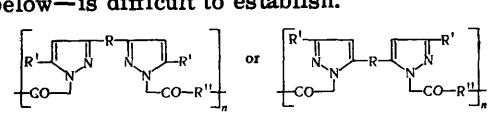
Heating polyacylhydrazones in an atmosphere of inert gas in a vacuum at 200–250°C for 3–5 h leads to the formation of polyacylpyrazoles in quantitative yield. Polyacylpyrazoles are yellow powders soluble in cresol, dimethyl sulphoxide, dimethylformamide, and sulphuric and formic acids.

Polyacylhydrazoles exhibit stability to hydrolysis by boiling water and to the brief action of conc. H_2SO_4. At room temperature polyacylpyrazoles are unchanged after several days action by 25% KOH solution; boiling for 12 h in the same alkali solution leads to complete destruction of the polymer. The bispyrazole formed as a result of hydrolysis is identical with the known product obtained from a ketone and hydrazine hydrate.

The production of bispyrazoles in the hydrolysis of polyacylpyrazoles with almost quantitative yield is confirmation of the structure of the polymers as linear macromolecules with repeated pyrazole rings. Proof of the correctness of the structure attributed to the polymers was also obtained in studying their ultraviolet and infrared spectra and also by counter-synthesis of the polyacylpyrazoles from bispyrazoles and acid chlorides of dicarboxylic acids[84–86]:



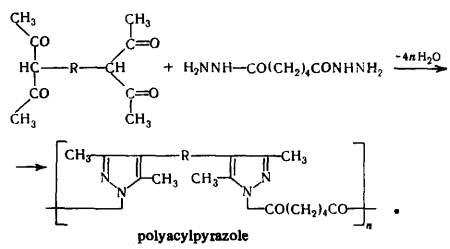
It is noteworthy that the precise position of the enol hydroxyl in bis-(β-diketones)—which determines whether the polyacylpyrazoles formed have one of the two structures shown below—is difficult to establish.



poly-1,3-pyrazole poly-1,5-pyrazole

However, Lowe and Ferguson[87] have shown convincingly that in benzoylacetone the carbonyl adjacent to the phenyl ring is enolised. Therefore of the two possible isomeric structures the poly-1,5-pyrazole structure must be considered the more probable, since linear bis-(β-diketones) can be considered to be analogues of benzoylacetone.

c. Branched bis-(β-diketones). The reaction of branched bis-(β-diketones) with hydrazides of dicarboxylic acids can be effected both in solution and in the melt. Branched bis-(β-diketones), as might have been expected, were much more reactive than the linear ones. 1,4-Bis-(2,2′-diacetoethyl)benzene, 4,4′-bis-(2,2-diacetoethyl)biphenyl, and 4,4′-bis-(2,2-diacetoethyl)diphenyl oxide exist predominantly in the ketonic form and react with adipic hydrazide very vigorously, forming polyacylpyrazoles directly under mild conditions; the intermediate polyacylhydrazones could not be isolated.

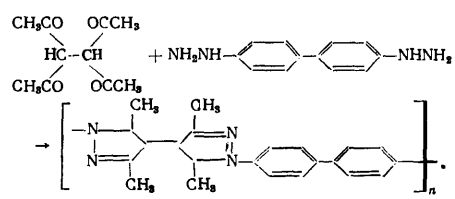


polyacylpyrazole

1,1,2,2-Tetra-acetylethane is an exception to the series of branched bis-(β-diketones), since it exists exclusively in the *cis*-enol form. On reacting with the hydrazide of adipic acid it forms a polyhydrazone comparatively readily, but attempts to cyclise this were unsuccessful. 1,1,3,3-Tetra-acetylpropane behaves similarly: it readily forms a polyhydrazone, which under different cyclisation conditions forms the same product, corresponding to a mixture of 50% polyhydrazole and 50% polyhydrazone.

According to the infrared and PMR spectra this ketone is 50% enolised[51]. However, tetra-acetylethane and tetra-acetylpropane readily form bispyrazoles with hydrazine hydrate, from which the corresponding polyacylpyrazoles were obtained by polycondensation with adipoyl chloride[85].

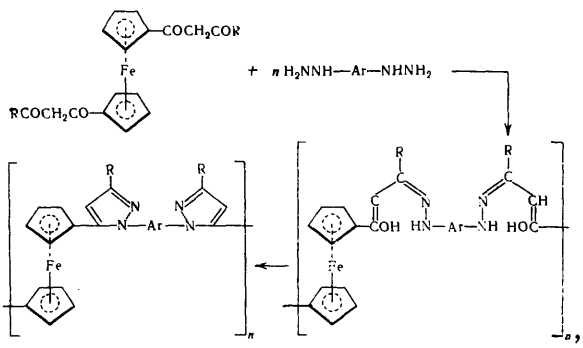
High-molecular-weight thermally stable polyarylenepyrazoles were obtained by heating bis-(β-diketones) with dihydrazines (for example, with 4,4′-dihydrazinobiphenyl). They exhibit high stability to hydrolysis by water and the action of acids and alkalis[88]. Their formation can be represented in general by the following scheme:



The structure of these polymers was demonstrated by the investigations of Mosby[55], and of Schaefer and Bertram[89].

By low-temperature condensation of 1,1′-bis(diketo)ferrocenes with aromatic or pseudoaromatic dihydrazines in solution, Neuse[90] obtained soluble polyhydrazones with a molecular weight of 1500–2000 and a viscosity of ~ 0.1–0.2 dl. g^{-1}. By thermal treatment at 200–240°C these polyhydrazones undergo cyclisation with the formation of

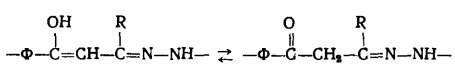
polymers containing pyrazole heterocycles substituted in positions 1 and 5:



where R = H, CH_3, C_6H_5; Ar = *m*-C_6H_4, *p*-C_6H_4, *p*-C_6F_4-C_6F_4-*p*, and *p*-C_6H_4-SO_2-C_6H_4-*p*.

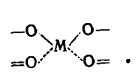
Infusible, but usually soluble, polypyrazoles had a reduced viscosity of 0.15–0.40 dl. g^{-1} and exhibited high thermal stability, exceeding that of other known ferrocene-containing polymers with heterocycles in chains[90].

The investigation of the infrared and electronic spectra of the polyferrocenylhydrazones shows the possibility of the existence in them of keto–enol equilibrium of the type:



and that the formation of a hydrazone includes the predominance of the γ-carbonyl groups of the initial bis-diketo-compound. When R = H the formation of a hydrazone takes place exclusively through the γ-carbonyl; the polymer has weak absorption in the 6.02–6.05 μm range, which is characteristic for aliphatic acyl derivatives of ferrocene in which the Φ–CO–CH_2 group is present. The additional vibrations at 5.75–5.80 μm which show the formation of a hydrazone through the α carbonyl are absent[90].

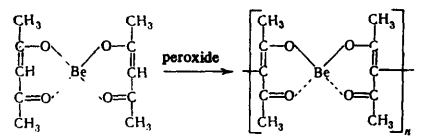
d. Coordination polymers based on bis-(β-diketones). Bis-(β-diketones) of various structure were used in polycoordination which led to the use for the construction of polymeric molecules of coordinate bonds, as well as the ordinary covalent bonds, and to the inclusion of metal atoms in the macromolecule. In this instance the bond between the metal and the ligand is effected through oxygen:



A large number of review articles and original papers deal with the synthesis of coordination polymers are the study of the polycoordination[91–99].

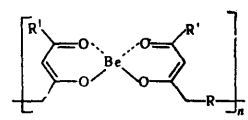
Metals with coordination number 4: copper, beryllium, zinc, magnesium, cadmium, calcium, and also transitional metals: nickel, cobalt, manganese, chromium, titanium, etc., have mainly been used for the synthesis of the coordination polymers.

The production of coordination-chain polymers can be brought about by the reaction of aqueous solutions of salts of the corresponding metals with alcoholic solutions of the bis-(β-diketones)[100] or by heating stoichiometric amounts of the metal acetylacetonate with the bis-(β-diketone) in vacuo or in a high-boiling solvent[101–103]. In the latter procedure the acetylacetone is liberated and a metal derivative of the original tetraketone is formed. Coordination polymers were also obtained by interfacial polycondensation (polycoordination)[104–106] and by polyrecombination of beryllium acetylacetonate[107]:

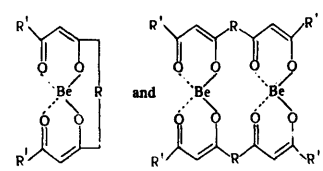


The coordination polymers obtained by the above methods are infusible and insoluble products, which makes it extremely difficult to investigate the mechanism for their formation, and to study their properties and field of application. The molecular weights of these polymers varied within the range 1000–5000, which impeded the appearance of the main polymeric properties: mechanical strength, and ability to form films and fibres.

The coordination polymers of the type:

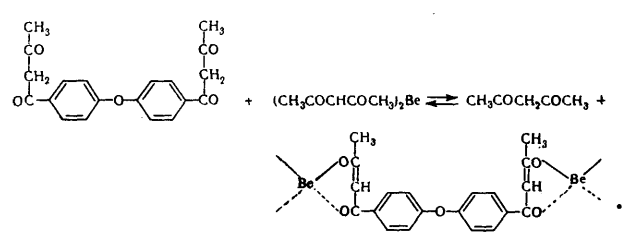


with the highest molecular weights were obtained by the polymerisation of cyclic coordination compounds of beryllium formed in the thermal destruction in vacuo of the low-molecular-weight coordination polymers of the corresponding bis-(β-diketones) and beryllium[13]:



where R′ = CH_3, CF_3; R = $[CH_2]_6$, $[CH_2]_7$, $[CH_2]_{10}$, $[CH_2]_{12}$, $NH[CH_2]_6NH$, $NH[CH_2]_{10}NH$, *p*-$[O(CH_2)_2O]_2C_6H_4$, $O[CH_2]_6O$ (R = CF_3).

The detailed investigation of polycoordination by the example of the reaction of 4,4′-bis(acetoacetyl)diphenyl oxide with beryllium acetylacetonate both in the melt and in solution allowed the main rules for this process to be established. It was found that polycoordination is a form of polycondensation process, which can be carried out at elevated temperature and which is an equilibrium process[101–117]:



Under polycoordination conditions the coordination polymers are capable of undergoing exchange reactions both with the low-molecular-weight product of the polycoordination (acetylacetone) and with low-molecular-weight substances which are similar in chemical nature to the coordination polymer (the acetylacetonate of another metal); exchange reactions also of individual polymeric molecules

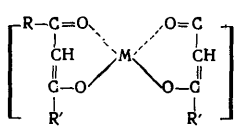
with one another also occur. Finding the main rules of polycoordination made it possible to obtain coordination polymers of high molecular weight[98,99].

A study of the kinetics of polycoordination of 4,4′-bis(acetoacetyl)diphenyl oxide with beryllium acetylacetonate in dimethylformamide solution and in Dinyl showed that this process is a second-order reaction with an activation energy of 25 kcal mole^{-1}.[109]

The properties of the coordination polymers, as for other types of high-molecular-weight compounds, are determined by the flexibility of the polymeric chain, the interfacial interaction, and the stereochemical regularity of the macromolecule. The ionic radius of the metal participating in the formation of the polymeric chain has a considerable effect on the strength of the interchain interaction and the packing density of the macromolecules of coordination polymers of the bis-(β-diketones). When the radius of the metal differs considerably from those of other atoms forming the chain (for the polymers of beryllium) this results in a disturbance of the packing density of the polymeric chains, a weakening of the force of interchain interaction, which in turn determines their best solubility and fusion[112].

The melting point of the coordination polymers of 4,4′-bis(acetoacetyl)diphenyl oxide, 4,4′-bis(acetoacetyl)diphenylmethane and 1,1,2,2-tetra-acetylethane with various metals decreases in the order: Be > Mg > Ca > Zn. The nature of the metal also affects the colour of the polymer[113].

The properties of the coordination polymers of the bis-(β-diketones) depend considerably on the chemical structure of the initial tetraketone, since in all the polymers of the bis-(β-diketones) the same coordination ring



is present, which is a comparatively stable formation in view of the fact that the donor groups coordinated with the metal ion occupy positions fixed relative to one another, the observable differences in the properties of these polymers are determined by the flexibility of the initial ligand and the packing density of the polymeric chains. The flexibility of the bis-(β-diketone) ligand will increase with increase in the number of methylene groups it contains, with decrease in the concentration of aromatic nuclei, with inclusion of aliphatic links between the aromatic nuclei of the tetraketone; the packing density of the polymeric chains will decrease on going from bis-(β-diketones) with aromatic nuclei substituted in the *para*-position, to bis-(β-diketones) with aromatic units substituted in the *meta*-position[99].

An increase in the flexibility of the polymeric chains or a decrease in their packing density owing to the corresponding changes in the structure of the initial bis-(β-diketone) is usually accompanied by a decrease in the thermal stability and an increase in the solubility of the coordination polymers[100,106,111,112].

An improvement in the solubility of the coordination polymers of the bis-(β-diketones) is brought about by the introduction into the ligand molecule of polar substituents on using a six-coordinated metal, four bonds of which participate in the creation of a coordination ring and two are occupied by aromatic radicals[118]. For example, the coordination polymers of terephthalyldiacetoacetic ester with copper, nickel, cobalt, magnesium, zinc, and mercury of the general formula:

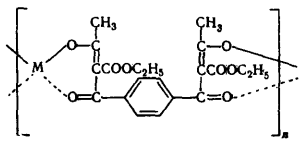
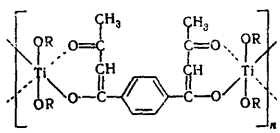


exhibit better solubility than the polymers of terephthalyldiacetone.

The coordination polymers of tetraethyl and tetra-t-butyl orthotitanates and terephthalyldiacetone of the structure



exhibited solubility in xylene[118].

The infrared spectra of polymeric copper chelates of bis-(β-diketones) have been studied[119].

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Institute of Organoelemental Compounds,
Academy of Sciences of the USSR,
Moscow

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Polyphosphazenes

V.V.Kireev, G.S.Kolesnikov, and I.M.Raigorodskii

Phosphazene polymers, their methods of production, properties, and uses are considered. A new classification for polyphosphazenes is proposed. 298 references.

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I. INTRODUCTION

The chemistry of the phosphazenes, derived initially from the work of Liebig[1], has shown considerable developments in recent years, due on the one hand to the scientific interest in this independent class of compounds and on the other to the great practical value of many phosphazene compounds, especially the polymers. A review[2] published in 1943 cited 73 references; the exhaustive review of Shaw and coworkers[3] published 19 years later had 397 references and after four more years the number of publications and communications in this region had increased almost twofold[4].

The reviews published earlier[2-10] did not contain thorough and critical considerations of the phosphazene polymers. The published reviews of phosphazene polymers[11-14] are restricted to an examination of the various types and classes of polyphosphazenes.

In recent years much new material on the synthesis, structure, and properties of polymeric phosphazenes has accumulated and shows the separation of this division of phosphazene chemistry into a separate branch of the chemical science of polymers, a branch which is of independent interest.

The present article is an attempt at a more detailed review of the latest approaches in the chemistry of phosphazene polymers without considering cyclic and linear oligomers and methods of obtaining them, and a new classification for these polymers is also proposed.

II. CLASSIFICATION OF POLYPHOSPHAZENES

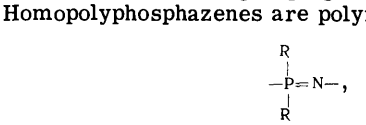
The first attempt at the classification of the phosphazene polymers was made by Shaw[15], who proposed to divide them into two classes: (1) polyphosphazenes obtainable by the polymerisation of cyclic phosphazenes; (2) polyphosphazenes obtainable by polycondensation; the latter, in turn, are subdivided into those which can be synthesised by the homopolycondensation of only phosphazene monomers (for example, phosphams) and the polycondensation of them with other monomers.

Another classification[4] is based on the nature of the substituents connected with the phosphorus atom in phosphazene polymers; according to this they are divided into purely inorganic (polyhalogenophosphazenes, polythioisocyanatophosphazenes) and organo-substituted phosphazenes. However, in using the above two classifications it is difficult to systematise all the various phosphazene polymers.

We think that the appearance in recent years of new and numerous types of phosphazene polymers enables the classification proposed earlier to be reconsidered and the classification adopted to be based on the structure of the macromolecule of the polymers and not on their method of production or the nature of their lateral substituents.

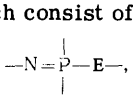
We think that the structural-chemical classification of high-molecular-weight compounds proposed by Korshak[16] is more correct in principle for systemising the polyphosphazenes. In accordance with this principle all the polyphosphazenes can be divided into three large classes: homopolyphosphazenes, heteropolyphosphazenes, and polymers with phosphazene groupings in the side-chain.

Homopolyphosphazenes are polymers of the type

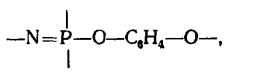


the main chain of the macromolecules of which is constructed from alternating phosphorus and nitrogen atoms, and the lateral radicals can be inorganic (halogens, isothiocyanate groups), or organic, or organoelemental. Examples of homopolyphosphazenes are the polydichlorophosphazene, polydimethylphosphazene, polydialkoxyphosphazenes, etc.

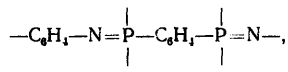
Heteropolyphosphazenes are polymers, the macromolecules of which consist of units of the type



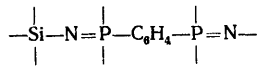
where E represents atoms or groups of atoms other than the phosphazo-group. Examples of the second class of phosphazene polymers include the polyoxyphenyleneoxyphosphazenes



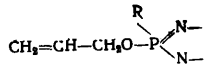
the polyphenylenephosphazenes



and the polyphenylenesilylphosphazenes



Polymers with phosphazene groupings in the side-chain contain macromolecules with a main carbo- or hetero-chain and phosphazene groups in the side-chain. Such polymers are obtained by the polymerisation of unsaturated organic derivatives of phosphazenes, for example:

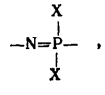


Our proposed classification of the polyphosphazenes is analogous to that generally accepted in the chemistry of organic and organoelemental polymers; it is mainly based on a constant criterion of these polymers—the structure of the macromolecules. This classification allows both the known phosphazene polymers and polymers which may appear in future to be systematised.

III. HOMOPOLYPHOSPHAZENES

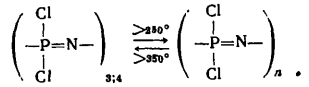
1. Polyhalogenophosphazenes

Linear polyhalogenophosphazenes are inorganic polymers with an elemental unit of the macromolecule of the structure



where X is Cl, Br, or F. These polymers are distinguished primarily by high thermal stability and fire resistance, although they are of limited practical use owing to low stability towards hydrolysis. Nevertheless the finding of the main rules for the formation of halogenophosphazene polymers always was and is still an extremely important task. A knowledge of these rules could open the path to the production of such linear polymers and rubbers with highly elastic macromolecules, combined with good thermal stability, materials which are needed by modern technology.

As long ago as 1870 Wichelhaus[17] observed the formation of a resinous substance on heating hexachlorocyclotriphosphazotriene (HCP). Later, Stokes[18] noted, in studying the polymerisation of cyclochlorophosphazenes with 6–12 atoms in the ring, that it proceeds very slowly at 250°C and rapidly at 350°C, while depolymerisation of the polymer starts at not much above 350°C:

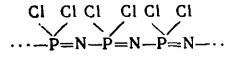


Stokes also noted the decomposition of polychlorophosphazene by hot water.

Schenk and Romer[19] observed the polymerisation of HCP and octachlorocyclotetraphospazotetraene (OCP) from 250° to 350°C and described the physical properties of the polychlorophosphazene rubber, which is colourless when pure, transparent, insoluble in organic solvents, but swells strongly in benzene and is stable in the cold to the action of inorganic acids. Under the action of water this polymer loses its elasticity, being converted into a brittle mass. It was also found that linear oily oligomers can also be converted into a rubber but below 200°C.

Renaud[20–23] studied the polymerisation of HCP and made an X-ray diffraction investigation of the polymers which are formed; according to his results these polymers had an amorphous or a crystalline structure. The effect of the polymerisation temperature on the molecular weight of the polymers formed was noted; their glass formation temperature was −47°C.

Detailed study of the physical properties of the polychlorophosphazene rubber were carried out by Meyer and coworkers[24–27]. Various polyhalogenophosphazenes were examined. Meyer[24] found the most probable position of the phosphorus and nitrogen atoms in the macro-chain. On the basis of the X-ray diffraction investigations of chlorophosphazene rubber, a fibrous structure was proposed for it, amorphous in the unextended state and crystalline when stretched. As was shown, the main valencies of the macromolecule



are arranged in a direction parallel to the axis of the fibre with an identity period of 5.16 Å, which corresponds with two elemental units.

The thermoelastic properties of the polychlorophosphazenes suggest the existence of spiral, flexible, long chains[25–27], with the molecular weight, calculated from the thermoelastic properties, equalling 20 000.

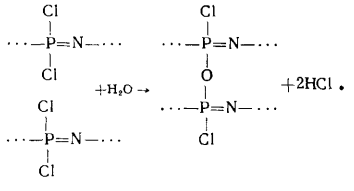
From the X-ray results the P–N–P bond angle in a rubber macromolecule was found to be equal to the N–P–N angle, 124°.[28] From its physico-mechanical properties, freshly-prepared chlorophosphazene rubber is not inferior to organic rubbers[26,27].

Ficquelmont suggested[29] that the polychlorophosphazenes consist of cross-linked macromolecules and the gradual decrease in their elasticity is connected with the crystallisation processes. When heated carefully to 500°C the rubber is converted into a black, infusible, insoluble product. Later[30], a tendency to a more rapid crystallisation of the polymerisation product from pure HCP than of the polymer from a mixture of low-molecular-weight homologues was observed.

In a subsequent paper Ficquelmont[31] noted that the polymerisation of cyclic chlorophosphazenes and the depolymerisation of the rubber are equilibrium processes. Schmitz-Dumont[32,33] concluded that in the polymerisation of HCP and OCP true equilibrium exists only in the gas phase. When cyclochlorophosphazene vapour was heated to 600°C a rubber was not formed, but a mixture of HCP, OCP, and higher homologues in crystalline and liquid states was obtained.

These results were confirmed by Moureu and Ficquelmont[34], who determined the molar heat of vaporisation on the elemental unit $PNCl_2$, equal to 15.5 kcal, and showed the impossibility of reaching high polymerisation coefficients in the gas phase.

Specker[35,36] investigated the physico-mechanical properties of the polychlorophosphazene rubber in the light of Kuhn's kinetic theory. The elasticity modulus was found to be proportional to the temperature in the range from −60° to 160°C, Specker found the elasticity modulus of rubber to be 2–4.2 kgf cm^{-2}. Values of the elasticity modulus close to these limits were also found later[37,38]. The molecular weight of rubber calculated by Kuhn's formula was 80 000, which corresponds to 700 $-PNCl_2-$ units. Specker considers[36] that the increase in the elasticity modulus of polychlorophosphazene is connected not with the crystallisation of the rubber but with the hydrolysis of the polymeric molecules and the formation of a lattice structure:



The first investigations of the kinetics of the thermal polymerisation of HCP were made by Schmitz-Dumont[33]. Systematic and detailed studies in this direction were made by Patat and coworkers[39–42].

Patat and Kolinskii[39] investigated the polymerisation of cyclic chlorophosphazenes in hydrocarbon solvents in the presence of oxygen at 250–350°C. They thought that the oxygen was responsible for the initiation of polymerisation, breaking of the chain, and the cross-linking of the macromolecule. However, it was found later[41] that polymerisation of sufficiently pure cyclochlorophosphazenes in the absence of oxygen takes place by a radical mechanism with homolytic breaking of the P–N bond in the ring as a second-order reaction with an activation energy of 42 kcal mole^{-1}.

Abel[43], who found that the reaction order of block polymerisation of cyclochlorophosphazenes is between 1 and 2, doubted the radical mechanism of this process.

Patat and Derst[42] found that depolymerisation of polychlorophosphazene rubber is a first-order reaction with an activation energy of 26 kcal mole^{-1} and a rate independent of the presence of oxygen. Nevertheless they stated that the depolymerisation had a radical character but with peculiarities connected with the structure of the rubber. They suggested that polychlorophosphazene is constructed from small cyclic molecules connected with one another. Such a structure for the rubber explains its high molecular weight and insolubility. In depolymerisation, as a result of the homolytic breaking of bonds these rings are freed from one another forming small cyclic molecules. The depolymerisation of higher linear halogenophosphazenes can generally be used as an effective method for obtaining the lower cyclic homologues[44,45], the yields of the individual phosphazenes decreasing with increase in the size of the ring, so the amounts of the cyclic tri-, tetra-, penta-, hexa-, and hepta-mers formed in the depolymerisation of the polychlorophosphazene are[44] in the ratio 20 : 15 : 8 : 5 : 1.

In investigating the block polymerisation of HCP at 275–350°C and the hydrolysis of polychlorophosphazenes Gimblett[46] concluded that polymerisation takes place in the gas phase by a radical mechanism and the breaking of the chain is effected in the block as a result of recombination. Chain-transfer reactions should also take place in the block through the polymer molecule with the formation of branch and lattice structures[46]. The effect on the thermal polymerisation of HCP of its concentration, the temperature of the process, and the reactor material has been shown[47]. The polymerisation is described by an S-shaped kinetic curve.

Shaw[48] suggested that if this reaction also involves free radicals their concentration is very low.

The radical mechanism of polymerisation came under even greater doubt after an investigation of the radical polymerisation of industrial HCP under the influence of γ-radiation[49] and of the polymerisation of pure HCP under the action of ultraviolet radiation[50] or of a beam of accelerated electrons[51], since in every instance of polymerisation either polymerisation was not observed or low-molecular-weight oligomers were obtained.

As is well known, cyclochlorophosphazene molecules contain P–N and P–Cl polar bonds. Therefore the initiation of polymerisation is probably connected with the heterolysis of some bond and the ionic initiation of chain growth. This view was first advanced by Konecny and coworkers, who studied the catalytic polymerisation of cyclochlorophosphazenes[52], and by Gimblett[53] who, in studying the thermal polymerisation of HCP, suggested that the act of initiation is the breaking of the P–Cl bond in HCP by the reaction:

$$P_3N_3Cl_6 \rightleftarrows P_3N_3Cl_5^+ + Cl^-,$$

and the chloride ion is responsible for the chain growth.

Further investigations of the electrical conductivity of HCP[54], its ability to form pyridinium salts[55] and pyridine complexes with Lewis acids[56] confirmed the suggestions about the possibility of heterolytic breaking of the P–Cl bond in HCP.

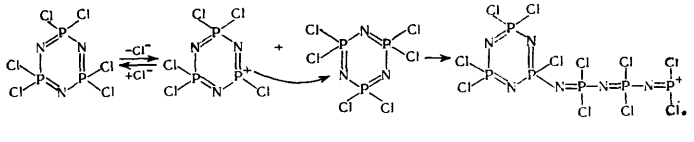
A study of the mechanism of thermal polymerisation of HCP with the aid of the EPR method and by measurements of the capacity, electrical conductivity, and dipole moments of HCP melts at various temperatures, also confirmed the ionic nature of the thermal polymerisation of the cyclochlorophosphazenes[57].

Table 1. Electrical conductivity of $(PNCl_2)_3$ and $[PN(OC_6H_5)_2]_3$, 10^{11} mΩ cm^{-1}.

$P_3N_3Cl_6$		$(PN(OC_6H_5)_2)_3$		$(PN(OC_6H_5)_2)_3$	
°C	conductivity	°C	conductivity	°C	conductivity
120	1.7	120	1.5	163.5	4.8
163	1.7	165	3.5	139	2.4
203	33	203.5	4.3	350	316
253	6250	252	17.7	120	17.7
202	2900				

Measuring the EPR in the range from 25° to 250° did not show free radicals in a melt of the trimer; the dielectric constant alters slightly under these conditions (from 2.52 to 4.85). However, the conductivity changes very sharply, especially above 200°C (Table 1). For comparison, Table 1 gives the change in conductivity of a control compound—hexaphenoxycyclotriphosphazotriene which does not polymerise in the temperature range studied[57].

These results convincingly support an ionic mechanism for the polymerisation of HCP. Unlike Gimblett's hypotheses[53], Allcock and Best[57] consider that the growth of the chain of cyclic cations is brought about by the positive charge on the phosphorus atom, which attacks a nitrogen atom of a new phosphazene ring, starting chain growth:



This mechanism also provides a reason for the formation of a three-dimensional polymer: the terminal group of the growing chain is a ring, which can also undergo electrophilic attack by the growing end of another macrochain, giving the beginning of branching.

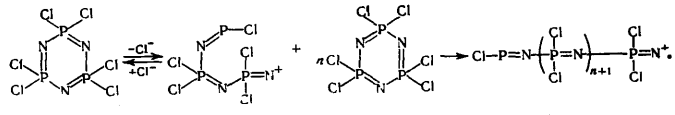
A mass-spectrometric study of the products of the decomposition of cyclochlorophosphazenes by Brion and Paddock[58] showed that a compound of ionic type $P_nN_{n+1}Cl^-_{2n+1}$ is formed predominantly.

Heterolysis of the P–Cl bond in linear molecules of polychlorophosphazenes is evidently also the reason for their depolymerisation at higher temperatures. It cannot be ruled out that this process can be effected at any part of the chain. The following results suggest that polymerisation and depolymerisation of chlorophosphazenes are equilibrium reactions[59]: (1) when held separately at 600°C the linear polychlorophosphazene and a mixture of the trimer with tetramer (HCP and OCP) both form a mixture of linear and cyclic chlorophosphazene oligomers of the same composition[33]; (2) with increase in the temperature the proportion of the polymer in the equilibrium mixture drops and that of the lower rings rises; (3) an increase in pressure favours the formation of a polymer[60]; (4) the polymerisation of cyclic chlorophosphazenes $(PNCl_2)_{3-7}$ is endothermic and ΔH_{polym} decreases with increase in the size of the ring, amounting to 1.39 kcal mole^{-1} for the trimer and 0 for the hexamer[61].

Evidently, as for other inorganic polymers the polymerisation of chlorophosphazenes and depolymerisation of polychlorophosphazenes includes an equilibrium between all the homologues $(PNCl_2)_n$ with n from 3 to 15 000 and the direction of the process is determined by the change in free energy $\Delta G = \Delta H - T\Delta S$, that is, by the change in the entropy and enthalpy of the system[62]. Kinetic factors must also be taken into account[63].

Probably the depolymerisation of polychlorophosphazenes takes place with participation of ionic terminal groups; possibly the high polarity of the bonds in the main chain of the macromolecules of the polychlorophosphazene also permits the rearrangement of the bonds, as is observed with the polysiloxanes[64].

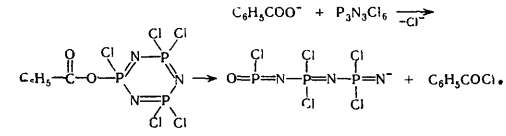
Konecny and Douglas[50] first observed the catalytic action of many organic compounds and metals in the polymerisation of cyclochlorophosphazenes. It was noted that the polymerisation of GCP is also brought about by t-butyl peroxide, but here the catalysis cannot be ascribed to the decomposition of peroxide into radicals, since at 210°C its half-decomposition period is very short whereas the polymerisation occurs in a few hours. The reaction also proceeds similarly in the presence of ammonium persulphate[65]. The investigation of the polymerisation of cyclochlorophosphazenes in the presence of benzoic acid, diethyl ether, and alcohols[52] suggested that the initiating act of chain growth is the heterolysis of HCP molecules (or other rings) at the P–N bond with formation of an active electrophilic centre at the nitrogen atom



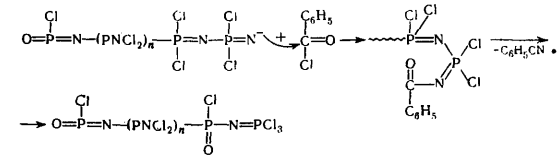
Gimblett found that oxygen does not affect the rate of catalytic polymerisation of HCP in the presence of benzoic acid; this polymerisation can be described by a first-order equation with an activation energy of 27.3 kcal mole^{-1}.[66]

A study of the kinetics of block polymerisation of HCP at 240–250°C showed it to be a second-order reaction with activation energy of 57 kcal mole^{-1}.[67]

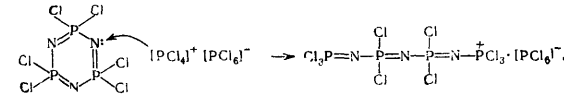
An investigation of the effect of benzoic acid and its salts on the polymerisation of HCP was made[67]. On the basis of the analysis of the volatile products of the polymerisation and of the previously established nature of interaction of salts of benzoic acid and HCP[68] it was suggested that the most probable mechanism includes attack by the benzoate anion on the HCP molecule and its opening by the scheme



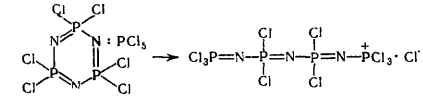
The linear anion formed reacts with HCP molecules starting the chain growth. The breaking of the chain is represented as follows:



This anionic mechanism is evidently specific for the action of benzoic and other carboxylic acids. Sometimes cyclochlorophosphazenes are polymerised in the presence of Lewis acids. The first report of the conversion of cyclic chlorophosphazenes into linear ones on heating with PCl_5, $AlCl_3$, $FeCl_3$, and other chlorides appeared in 1959.[69] Later it was stated in a patent[70] that such a process is brought about by heating cyclochlorophosphazenes in an autoclave at temperatures above 250°C with various iron, phosphorus, aluminium, and antimony chlorides, etc. After Becke-Goering and coworkers[71,72] had established the structure and mechanism of formation of linear chlorophosphazenes, the nature of the processes thus occurring became evident, which for PCl_5 can be represented as follows. Cyclochlorophosphazene (for example, HCP) are attacked by the $[PCl_4]^+$ cation with opening of the ring:

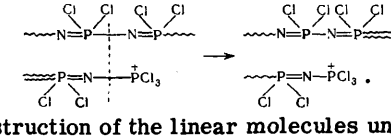


Chain growth takes place similarly with attack by a linear growing cation of the cyclic molecules until disappearance of the cyclophosphazene. Ring opening may precede its formation of a complex with PCl_5:



Here there is a chloride anion instead of a hexachlorophosphate anion. With other chlorides there is evidently similar opening of the rings[73].

Probably the terminal cationic groups of linear molecules react not only with cyclic molecules but also with linear macromolecules especially after the chlorophosphazenes have been used up:



This destruction of the linear molecules under the action of the terminal groups will, as for many polycondensation organic polymers, lead to the formation of an equilibrium mixture containing linear and cyclic chlorophosphazenes[74].

Even in the preparation of chlorophosphazenes by the ammonolysis of PCl_5 part of the linear oligomers can split off cyclised short-chain fragments [75].

Above 250°C equilibrium is reached rather rapidly—after 1–2 h. [70] The amount of chloride in the reaction mixture will determine the molecular weight of the linear chlorophosphazenes which are formed.

Considering the above possibility of polychlorophosphazene distribution as a result both of terminal group reactions and the intrachain rearrangement of bonds, the possibility of interchain exchange leading to the formation of an equilibrium mixture of linear molecules must also be admitted. Catalytic breaking of the macromolecules under the action of other reagents, for example, chlorine, is also possible at the same time.

The ability of phosphorus, aluminium, and iron chlorides etc. to stabilise linear chlorophosphazenes is sometimes used in the preparation of chlorophosphazenes by the ammonolysis of PCl_5. The ammonolysis was carried out in the presence of these chlorides [77,78] or even in the presence of metals [79–81] which form chlorides during ammonolysis.

The mechanisms of the thermal and catalytic polymerisation are thus very similar, especially at the chain growth stage--in every instance this is the process of growth of a polymeric ion.

Among other methods of polymerisation mention must be made of attempted solid-phase polymerisation of HCP and OCP. [82,83] Although radiation polymerisation of HCP does not take place [49–51], irradiation of the solid trimer with 50 kV X-rays at 40–120°C leads to the formation of a polymer [83]. However, the rate of polymerisation is low and reaches a maximal value of 0.8% h^{-1} at the melting point of HCP. By the action of γ-radiation for 300 h and a dose of 10^6–10^7 roentgen a degree of conversion of HCP into polymer of ~ 15% could be reached, which decreases in the presence of water, oxygen, solvent, and even OCP. [82] Unlike HCP the tetrameric chloride is not polymerised under the action of X-rays and γ-radiation. This difference in their capability for radiation polymerisation is evidently connected with the structural features of HCP (the greater capability of HCP for polymerisation was noted earlier [41]) and agree well with the calculated heat of polymerisation [61]. The identity of the polymers obtained by thermal and radiation polymerisation of HCP has been noted [82]. In the common solid-phase polymerisation of isomorphous HCP and hexabromocyclotriphosphazotriene the rate of polymerisation is lower than during their separate polymerisation [84].

It should be noted that in the determination of the quantitative rules for the polymerisation of cyclic chlorophosphazenes there are significant differences in the results of different authors (Table 2) even when the polymerisation is carried out under identical conditions. This characterises the complexity of the process of polymerisation of cyclochlorophosphazenes and the influence of many factors on this process.

Assuming that the most accurate values of the activation energy for the polymerisation of trimeric cyclochlorophosphazene is 27.3 kcal $mole^{-1}$ [66] and that for depolymerisation is 26 kcal $mole^{-1}$, [42] Paddock [10] considers that their difference accurately corresponds to the molar heat of polymerisation of HCP (1.39 kcal $mole^{-1}$), determined by differential thermal analysis [61].

There have been some reports of the polymerisation of oily homologues of chlorophosphazenes which also form chlorophosphazene rubber when heated above 130°C. [18,85,86] However, in estimating their polymerisation tendency it is necessary to take into account that these homologues can contain higher cyclic chlorophosphazenes with terminal NH groups [85] capable of polycondensation with liberation of HCl [86] and also that partial hydrolysis by small quantities of water with the formation of high-molecular-weight compounds in which the chlorophosphazene blocks are linked by P–O–P bonds can occur [85,87]. Linear polychlorophosphazenes with terminal ionic groups of the $\ldots P^+Cl_3.An^-$ type are thermally stable; their molecular weight does not change up to the depolymerisation temperature (although destruction processes with participation of terminal groups can occur in it). If these linear chlorophosphazenes have a low molecular weight and are not capable of being cyclised they are stable to temperatures above 500°C. [77]

Table 2. Results of the kinetic investigations of the polymerisation of hexachlorocyclotriphosphazotriene and depolymerisation of polydichlorophosphazene.

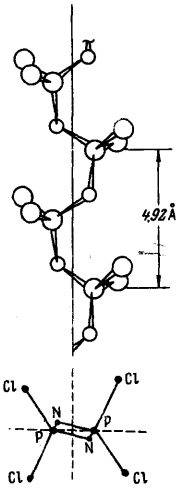
Process	Temp., °C	Kinetic order of reaction	Activation energy, kcal $mole^{-1}$	Reference
Polymerisation in the absence of air	250—300	2	42	41
Depolymerisation (traces of oxygen)	250—500	1	26	42
Polymerisation in benzene in the presence of various catalysts	210	1	—	52
Polymerisation in the presence of benzoic acid	200—210	1	27.3	66
Polymerisation in a block	240—255	2	57	67
Polymerisation in the presence of benzoic acid and sodium benzoate	235	1	—	67
Polymerisation in a block	250—300	1	51	47

An original method for obtaining linear polychlorophosphazenes was developed by Yakubovich and coworkers [88–90]. Heating low-molecular-weight linear compounds of the type $Cl[PNCl_2]_n$–$P(O)Cl_2$ and $R[PNCl_2]_n$–$P(O)Cl_2$ (where R is Cl, OR, or other groups and $n \geq 1$) at 150–200°C leads to the release of $POCl_3$ and the formation of a linear chlorophosphazene polymer of the general formula $P_XN_XCl_{2X}$ - mR_m free from lateral intermolecular bonds which are present in the polymers obtainable by thermal polymerisation of cyclochlorophosphazenes.

Since the hydrolytic stability of polychlorophosphazene is low, an attempt was made to improve it by various additions and modifiers, for example, silicone rubber, barium and tin stearates, and other salts [91] and also by carrying out the polymerisation of HCP in the presence of 2,6-di-t-butyl-*p*-cresol [92]; although in the last instance the hydrolytic stability of the polychlorophosphazene was increased ten times it was still unsatisfactory. The molecular weight of the linear polychlorophosphazenes was determined by various methods: by osmometry and viscometry [39–42], by viscometry and light scattering [93], and also from the temperature dependence of the elasticity modulus [35,36]. A comparison of the values of the osmometric and viscosimetric measurements made by Patat and coworkers [39,41] gave the following relation for solutions of polychlorophosphazenes in toluene: $[\eta] = 0.165 \times 10^{-4} M^{0.69}$. The values of the molecular weights of the polychlorophosphazene calculated by this formula were [41] ~ 10^6. Later [93] in an investigation of polychlorophosphazene isolated by precipitation into several fractions other values of the coefficients K and α in the equation $[\eta] = KM^{\alpha}$ were found for this polymer: in toluene $K = 3.89 \times 10^{-3}$ and $\alpha = 0.71$; in chloroform $K = 1.32 \times 10^{-1}$ and $\alpha = 0.56$. The difference between the values of the constants and those found earlier [99,41]

were explained[99] by the polydispersity of the products which Patat and coworkers had used. Nevertheless the absolute values of the molecular weights of the polychlorophosphazenes found by various authors agree satisfactorily and are ~ 10^5.

X-Ray diffraction studies of the polychlorophosphazene[94] suggested that its macromolecules do not have a spiral structure[27] but are almost planar. The conformation of the chain (see Figure) of the polychlorophosphazene is characterised by angles of rotation around the P–N and N–P bonds of 156° and 4° respectively, which is close to a *cis*-planar conformation. The identity period is 4.92 Å and includes two $PNCl_2$ links; the bond angles are PNP = 127° and NPN = 119° the length of the P–N bond is 1.74 Å.



Space model of a linear polychlorophosphazene.

Other halogenocyclophosphazenes are also capable of thermal polymerisation. At 250°C or over bromocyclophosphazenes form elastomeric products[95-97] which when heated subsequently form a brittle solid substance stable to the action of acids and alkalis. Polyfluorophosphazenes[98,99] form cyclofluorophosphazenes on heating above 300°C.

Of the other methods for making polyhalogenophosphazenes mention must be made of the "azide" method, which is being greatly developed. Thus, by heating PBr_3 with sodium azide at 170°C in the absence of a solvent, Herring[100] obtained polybromophosphazene:

$$PBr_3 + NaN_3 \xrightarrow{-NaBr} Br_2PN_3 \xrightarrow{-N_2} 1/n\,[-PNBr_2-]_n,$$

which forms an elastomer when heated to 200°C.

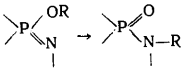
2. Polyorganophosphazenes

The chemical inertness of the P–C, P–O–C, and other bonds and above all their hydrolytic stability suggests that thermostable and chemically stable polyorganophosphazenes with these bonds in the side-chain can be obtained.

Two synthetic paths for such high-molecular-weight polymers are possible in principle: polymerisation of cyclic organophosphazenes and the replacement of the halogens in the polyhalogenophosphazenes by corresponding groups.

Polymerisation of cyclo-organophosphazenes. Most of the investigations in this field relate to attempts to polymerise alkyl, aryl, alkoxy, and aryloxy-cyclophosphazenes. Lipkin tried to convert the most accessible and easily obtainable in high yields of the alkoxy- and aryloxy-cyclophosphazenes into linear polymers[101]. By heating the products of the condensation of cyclochlorophosphazenes with phenoxides, alkoxides, and their thio-analogues, Lipkin obtained water-resistant polymers insoluble in organic solvents. Braun[102] repeated Lipkin's experiments but was unable to isolate pure products. When the aryloxyphosphazenes he had obtained were heated above 320°C their viscosity increased, they lost their solubility, but their composition did not change. Braun suggested that here polymerisation of cycloaryloxyphosphazenes took place with the formation of linear polymers.

Study of the thermal polymerisation of alkyloxy- and aryloxy-cyclophosphazenes in air and in nitrogen at 150–350°C showed that under these conditions low-molecular-weight polymers are formed[103]. Many authors[3] have noted the resinification and formation of polymeric products when alkoxycyclophosphazenes are heated in a vacuum, but it was found later[104] that the formation of polymers on heating alkoxycyclophosphazenes is due to side-reactions connected with the insufficient purity of the monomers. Shaw and coworkers[105-107] showed that at 200°C and above cyclic alkoxyphosphazenes undergo the phosphazene–phosphazane rearrangement:



but here there is no polymerisation as a result of the opening of the phosphazene ring, as occurs with halogenocyclophosphazenes. This is also characteristic for cyclophosphazenes with alkyl and aryl substituents at the phosphorus atom.

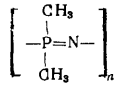
One of the first attempts at the polymerisation of the aryl-cyclophosphazenes was made by Bode and coworkers[108,109]: heating $(C_6H_5)_4P_3N_3Cl_2$, $(C_6H_5)_2P_3N_3Cl_4$ and $(C_6H_5)_6P_4N_4$ at 250–300°C for several hours leads, in their opinion, to the formation of polymers, but these polymers do not exhibit rubber-like properties. However, detailed investigation of the thermal polymerisation of $(C_6H_5)_6P_4N_4$ in the temperature range from 320° to 500°C showed[110] that there is hardly any polymerisation but a mixture of lower cyclic phenylphosphazenes is formed. The cyclic $(CH_3)_6P_3N_3$ and $(CH_3)_8P_4N_4$,[111] and $(C_2H_5)_6P_3N_3$ and $(C_2H_5)_8P_4N_4$[112] also do not polymerise on heating but start to decompose at 350–400°C. Similar results are also obtained in the polymerisation of the isopropyl- and phenyl-phosphazenes in air and in nitrogen[113].

Only two instances are at present known of the formation of high polymers from substituted cyclophosphazenes: at 150°C the trimeric and tetrameric isothiocyanate cyclophosphazenes form rubbery polymers[114-116]; tris-(*o*-phenylenedioxy)cyclotriphosphazatriene and tris-(2,2-dioxybiphenyl)cyclotriphosphazatriene also polymerise on heating[117,119].

Gimblett[53] thinks that the ability of thioisocyanatocyclophosphazenes to polymerise is due to the possibility of the ionisation of the P–NCS bond. However, as was correctly noted by Shaw and coworkers[120], both polymerisation as a result of the breaking of the phosphazene rings and also polymerisation with participation of thioisocyanato-groups

are possible here and it is still not yet known which of these two processes actually takes place. The same can also be said in respect of tris-(*o*-phenylenedioxy)- and tris-(2,2-dioxybiphenyl)-cyclotriphosphazotrienes: in addition to the polymerisation of the phosphazene rings[119] opening of the five-membered heterocycles is also possible and this can lead to the formation of polymers constructed from compounds with oxyaromatic units of substituted phosphazene structures.

Hence the direct thermal polymerisation of organocyclophosphazenes cannot yet be used for obtaining the corresponding homopolyphosphazenes. The catalytic polymerisation of these compounds shows greater promise. Rice and coworkers[121] heated a mixture of $(CH_3)_2P(NH_2)_2Cl$ and NH_4Cl and obtained the polymer



with a molecular weight of ~ 12 000, together with the corresponding trimer and tetramer. They suggest that the polymer is formed by the proton-catalysed polymerisation of cyclic phosphazenes. Polydimethylphosphazene is a crystalline polymer stable on heating to 300°C.[121]

It can be assumed that in the future the ionic polymerisation of many organocyclophosphazenes will be effected.

Synthesis of polyorganophosphazenes from polyhalogenophosphazenes. The reactivity of the halogens in the polyhalogenophosphazenes allows them to be readily replaced by various radicals.

The first attempt in this direction was made in 1948 when, by the action of alcohols in the presence of pyridine on polychlorophosphazenes with a polymerisation coefficient of 200, Goldschmidt and Dishon[122] obtained the corresponding polyalkoxy-derivatives, however, not all the chlorine was replaced, the proportion of alkoxy-groups was low and could not be increased by replacing the alcohol–pyridine mixture by alkoxides. Becke-Goering and Koch[85] obtained the corresponding polymethoxyphosphazene by the action of sodium methoxide on a linear chlorophosphazene oligomer with a polymerisation coefficient of 11. High-molecular-weight organo-oxyphosphazenes have been obtained by the action on polychlorophosphazenes of a mixture of alcohols and pyridine[123-126], alkoxides of alcohols and phenoxides[127-130], glycols or alkoxides of glycols[131,132].

The alcoholysis of polydichlorophosphazene favours its dissolution[125] or swelling[127] in an inert solvent. Under these conditions 93–95% of the chlorine atoms could be replaced by alkoxy-groups and polyalkoxyphosphazenes stable to hydrolysis obtained. The action of solutions of alkoxides or phenoxides in alcohol and also of amines[133] on polychlorophosphazene in benzene[129] gave the corresponding polyalkoxy-, aryloxy-, and amino-phosphazenes with high molecular weights. It was found that the process is not accompanied by appreciable destruction of the main chain of the initial polychlorophosphazene (see Table 3). X-Ray structural investigation of oriented linear alkoxy- or aryloxy-phosphazenes showed the identity period of their chains to be 4.8–4.92 Å, on the basis of which they were assigned a planar zig-zag structure[129]. With the aim of obtaining polymers which were more inert chemically, fluorinated[125-127,130,134] or chlorinated[124,128] alcohols were used for the alcoholysis of the polychlorophosphazenes, and polyalkoxyphosphazenes can be obtained by polyreesterification of the lower alkoxy-derivatives[125]. All the alkoxy-, aryloxy, and aminophosphazene polymers prepared exhibit comparatively low thermal stability—at 150–200°C and above they rapidly undergo destruction with the formation of low-molecular-weight linear and cyclic oligomers[129].

The greater ability of the high-molecular-weight organophosphazenes to undergo depolymerisation in comparison with the polychlorophosphazenes was related by Allcock[119,135] to the structure of the chain and the increase in the intramolecular interaction on replacing chlorine by larger organic radicals, which makes the cyclic compounds more stable thermodynamically. However, it is possible that the high flexibility and polarity of the bonds of the polyphosphazene chains[27] can also facilitate the destruction of the macromolecule and the formation of cyclophosphazenes, owing to the intramolecular redistribution of bonds, analogous to that observed in polyorganosiloxanes[64].

Polydimethylphosphazene could also be obtained by the action of CH_3MgBr or CH_3Li on polychlorophosphazene[136].

Table 3.

Elementary unit of the polymer	Mol. wt. $\times 10^{-3}$	T_c, °C	Solvent
$PN(OC_2H_5)_2$	2 000	—84	ethanol
$PN(OCH_2CF_3)_2$	1 700	—66	ketones
$PN(OC_6H_5)_2$	3 700	—8	benzene
$PN(OCH_3)_2$	640	—76	methanol
$PN(NHC_6H_5)_2$	1 650	91	benzene
$PN[N(CH_3)_2]_2$	363	—4	aqueous solution of acid
$PN(NC_5H_{10})_2$	697	19	benzene

Other methods of making polyorganophosphazenes. Methods of obtaining polyorganophosphazenes are known which are based on the use of alkali metal azides. This method was first proposed for obtaining chlorophenyl[100] and perfluoromethyl[137] polyphosphazenes and then extended also to phenyl polyphosphazenes[138,139]:

$$R_2PX + MN_3 \rightarrow [R_2PN_3] \rightarrow 1/n\,[-R_2P=N-]_n + N_2.$$

When R = CF_3 only a polymeric, solid, waxy product with a softening point of 95°C and good resistance to strong acids and oxidants is formed[137]. When R = CH_3 lower cyclic homologues are mainly formed.

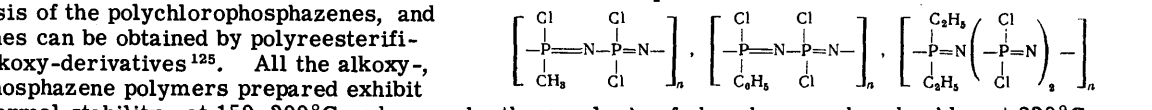
Linear oligomeric fluorine-containing organophosphazenes with yields of up to 40% (remainder: cyclic phosphazenes) are formed by the following reaction[140]:

$$R_2PNH_2 + Cl_2 \rightarrow R_2PCl_2(NH_2) \xrightarrow{R'_3N} 1/n\,[-R_2P=N-]_n + R'_3N \cdot HCl.$$

The polyfluoromethylphosphazene obtained by this method is similar to those made by the azide method[137]. By heating hydrazinophosphines at 200°C mixed polyarylaminoalkylphosphazenes of the formula:

were obtained[141].

Yakubovich and coworkers[142] obtained insoluble polymers of the composition

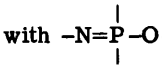


by the pyrolysis of phosphazene phosphoxides at 220°C.

IV. HETEROPOLYPHOSPHAZENES

In this class of polyphosphazenes we put the polymers which contain a main chain of phosphazene groups or structures linked by various organic, organoelemental, or inorganic radicals and groups of atoms:

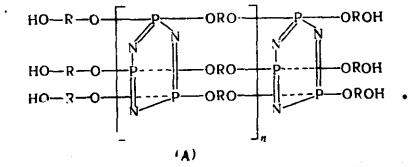
where E is alkylene, arylene, oxyalkyleneoxy, or oxyaryleneoxy radicals, residues of amines, diamines, the –NH– and O–B– groups, etc.

1. Polymers with  Bonds in the Main Chain

This type of heteropolyphosphazenes obtained on the basis of cyclic and linear halogenophosphazenes and polyoxy-compounds is one of the most promising polymers in practical respects, similar in structure to phenolic resins but differing from them by higher thermal stability and fire resistance.

Three methods for obtaining such polymers are now known[143]: the reaction of chlorophosphazenes with dihydricphenols[144-147], with phenoxides of diphenols[148,149] and the polyre-esterification of alkoxyphosphazenes with polyhydric phenols[150-152].

Although the reaction of chlorophosphazenes with alcohols and phenols has long been known[3], the preparation of polymers based on chlorophosphazenes and polyhydric phenols was first patented by Redfarn in 1957[144]. This method involved heating (at 170–190°C) a mixture of crystalline chlorophosphazenes, predominantly the trimer and tetramer, with resorcinol, hydroquinone, 2,2-di-(4-hydroxyphenyl)propane and other aromatic polyhydroxy-compounds, amounting to 75–100% of the weight of the chlorophosphazenes. The process was accompanied by the release of HCl and the formation of a resin capable of solidifying when heated with paraform or hexamethylenetetramine. However, the resins thus formed have low solubility owing to the high functionality of the original chlorophosphazenes; furthermore, the high temperature of the process facilitates the partial destruction of the phosphazene rings in these resins by the action of the HCl liberated. These drawbacks could be avoided by carrying out the polycondensation of the initial substances in organic solvents at temperatures below 130°C in the presence of acceptors of HCl—tertiary amines[145-146]. The use of an excess of dihydricphenols and their restricted solubility in the reaction mixture leads to gradual successive replacement of the chlorine atoms in the cyclochlorophosphazenes and the formation of resins predominantly containing structure of the type (for HCP):



(A)

However, these resins nevertheless contain up to 10% residual chlorine and are often sparingly soluble. The molecular weight of the soluble resins varies within the range 10 000–15 000; they are freed from traces of tertiary amines by precipitation with aqueous solutions of acids[153] and harden when heated with substances which are donors of formaldehyde[154] or in the presence of organosilicon or organotin hardeners[155].

An investigation of the reaction of HCP with dihydricphenols[143,147,156-158], made with the aim of finding the optimal conditions for the formation of polymers based on them showed that when pure the initial substances hardly react below 180°C whether in the melt or in organic solvents. Appreciable reaction starts above 190°C and its rate depends significantly on the polarity of the medium which also affects the composition and structure of the reaction products when the reaction is carried out in the presence of tertiary amines[143,156-158].

The order and rate constants of the reaction of equimolecular amounts of HCP and dihydricphenols were determined and it was assumed that both without catalysts and in the presence of tertiary amines the reaction is unimolecular with heterolysis of the P–Cl bond[157]. This assumption agrees well with the formation of pyridine complexes of HCP and $SnCl_4$ [56] and of phosphazenepyridinium salts[55].

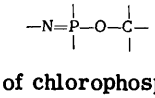
Bispentachlorocyclotriphosphazetrienes—the simplest homologues of the polyphosphazenes being considered—were isolated from the products of the reaction of equimolecular amounts of HCP and dihydricphenols by liquid absorption chromatography and characterised[159]. Their study allowed some conclusions to be drawn concerning their mode of formation[157,158].

To obtain only soluble resins, equimolecular amounts of cyclochlorophosphazenes and dihydricphenols were made to react and then the chlorine atoms left in the oligomers were replaced by various groups of atoms and radicals[160,161].

For the same purpose the functionality of the initial substances can be reduced by using monohydric phenols instead of the dihydricphenols[162] or by replacing some of the chlorine atoms in the original cyclochlorophosphazenes by inert phenyl[163-165] or phenoxy[166,167] radicals. Thus linear polymers with a softening point of 110–120°C and molecular weight of ~ 12 000 are obtained by heating dichlorohexaphenylcyclotetraphosphazotetraene and resorcinol in a vacuum at 310°C; when hydroquinone is used under the same conditions the molecular weight of the polymer is 5000.[163] Polymers of higher molecular weight were obtained from the same cyclophosphazene and 4,4-dihydroxydiphenyl oxide; the molecular weight of the polymer before purification was 42 000 when the reaction was effected in a melt and 115 000 when in a solvent; the molecular weights of the other fractions exceeded 250 000–500 000.[164]

Yokoyama and coworkers[168] repeated Redfarn's experiments[144] and also obtained resins insoluble in most solvents. The use of 2,6-bishydroxymethyl-*p*-cresol[169,170] leads to the formation of polymers similar to those described above. It was found that up to 200°C only the hydroxymethyl groups react with cyclochlorophosphazenes[169] but above 200°C the phenolic OH groups also start to react; homocondensation of the hydroxymethyl groups does not occur[170].

The release of HCl and the presence in the resinous products of some residual chlorine are the principal drawbacks of the method of making the heteropolyphosphazenes with



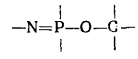
bonds by the reaction of chlorophosphazenes with polyhydroxycompounds. These drawbacks can be circumvented by the use instead of chlorophosphazenes of their alkoxy-derivatives[150-152]. The kinetics of the polyre-esterification of hexabutoxycyclotriphosphazotriene with diphenols was investigated and it was shown that the polymers thus formed are analogous to those synthesised from cyclochlorophosphazenes[152].

Instead of the completely substituted alkoxycyclophosphazenes, phosphazene compounds of the general formula

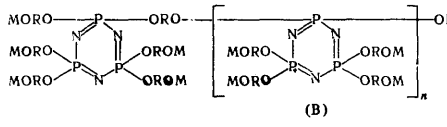
$$[PN(OR)_m(OH)_{2-m}]_n,$$

where $m \leqslant 2$, n is an integer $\geqslant 3$, and R = CH_3, C_2H_5, or C_4H_9, which are made by the alcoholysis of cyclochlorophosphazenes with lower alcohols, also react with diphenols. When these phosphazenes condense with dihydroxy-compounds water-soluble polymers are formed[171] which contain OH groups connected with phosphorus atoms. Such polymers can also be obtained by the hydrolysis of resins with cyclic phosphazene structures which contain residual P–Cl bonds[172,173].

An extremely promising method for obtaining polyphosphazene polymers with



bonds is by the reaction of chlorophosphazenes with phenoxides of polyhydric phenols[148,149], which are distinguished by a high rate even at comparatively low temperatures. Thus the reaction of HCP with the diphenoxide of 2,2-di-(4-hydroxyphenyl)propane dispersed in dioxan or ethyl methyl ketone ends after 2–4 h and leads to the formation of soluble and insoluble resins of type A (p. 67). When HCP reacts with an excess of diphenoxide in a medium which is a solvent for both the initial components (in alcohols) then polymers of type (B) are formed[149] (M = Na or K):

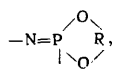


(B)

After the replacement of the phenoxide groups in these products by OH groups resins analogous to those of the phenol formaldehyde type are formed. The reaction of cyclochlorophosphazenes with diphenoxides is accelerated in the presence of pyridine or NaI.[174]

The resins of type (B) and also of type (A) readily harden when heated substances which are donors of formaldehyde; they are also convenient materials for modification or for preparing other polymers based upon them. Thus resin of type (A)[146] is used for the modification of butadiene–acrylonitrile copolymer[175] and resin (B) with phenoxide groups is readily epoxidised with epihalogenohydrins and forms epoxide phosphazene resins[176]. The latter were also obtained by the epoxidation of hexahydroxyarylene-hydroxycyclophosphazotrienes[177,178] (which are synthesised from the monophenoxides of dihydric phenols and HCP[179]) or on using the glycidyl ester of HCP;[180] nevertheless the attempt to obtain such esters by the epoxidation of allylhydroxyphosphazenes with peracetic acid was unsuccessful[181].

In the reaction of cyclochlorophosphazenes with dihydroxy-compounds (especially with glycols), in addition to the polymeric products, substances with a spirane structure are formed with a phosphorus atom in the alcoholic groups:



and partial dehydration of the glycols also takes place[182]. Thus in the reaction of *o*-diphenols (particularly pyrocatechol) with HCP or OCP in tetrahydrofuran in the presence of $(C_2H_5)_3N$[183] or in pyridine[184] a certain proportion of tris- or tetrakis-(*o*-phenylenedioxy)cyclophosphazenes is formed. It is interesting that these substances are capable of forming inclusion compounds with the molecules of various substances[185].

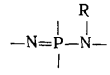
Other cyclic esters were synthesised from HCP and OCP with diphenols such as 2,2-dihydroxybiphenyl, toluene-2,3-dithiol, and 2,3-dihydroxynaphthalene[117].

The ability to form rings is much greater in the reaction of cyclochlorophosphazenes with glycols and other polyfunctional aliphatic compounds[186,187]. An increase in the [chain length of the] aliphatic radical between the OH-groups of glycol decreases the probability of the formation of spirane structures. This is especially noticeable in polyalkylene glycols[188–191]; when these are used polymeric products which can be employed in the production of polyurethane foams are formed[189–191]. This same effect is obtained when part of the chlorine in the initial cyclochlorophosphazenes is replaced by phenoxy-groups[192] or by perfluoroalkylphenol residues[193]. When glycols or amino-alcohols are used ring closure can proceed at different phosphorus atoms of the cyclophosphazene[194].

Phosphazene polymers based on aromatic polyhydroxy-compounds exhibit high thermal stability and fire resistance: they withstand long heating in air at 300°C[195] and can be heated to 500° for a short time[171]; in several instances destruction begins with breakdown of the phosphazene cyclic structures[164]; these polymers are also stable to attack by various chemical agents[145].

2. Heteropolyphosphazenes with –N=P(–)–N Bonds in the Main Chain

Polymers with



bonds in the main chain of the macromolecules (R = H or an organic radical) are obtained from chlorophosphazenes and ammonia or organic amines. The simplest representative of this class of polyphosphazenes—phospham—was first obtained by passing ammonia over molten HCP or by heating HCP with NH_4Cl.[196]

In investigating the ammonolysis of chlorophosphazenes Moureu and Rocquet[197] showed that on heating the prepared aminophosphazenes the irreversible loss of ammonia takes place and a polymeric product is formed—phospham:

$$[PNCl_2]_n + 4n\,NH_3 \xrightarrow[-2n\,NH_4Cl]{} [PN(NH_2)_2]_n \xrightarrow[2n\,NH_3]{} [PNNH]_n.$$

Phospham is an infusible powder which in the early stages of its formation can be dissolved in water; it is thermally stable up to 550–600°C and is converted into $(PN)_x$ on heating above 800°C. To accelerate the formation of phospham pyrolysis of aminophosphazenes is effected in the presence of NH_4Cl with passage of dry HCl.[198]

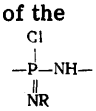
Audrieth and Sowerby[199,200] studied the formation of phospham from cycloaminophosphazenes by a thermogravimetric method. They found that the phosphams which are formed cannot be characterised by starting from the size of the phosphazene ring from which they were obtained. X-Ray structural investigations showed that the phosphams are amorphous substances and Steger[201] was unable to determine by infrared spectroscopy whether the size of the phosphazene rings was unchanged. He concluded that the phosphams are constructed from a disordered array of phosphazo-groups connected by –N= and –NH–structural elements.

The more detailed investigations of Miller and Shaw[202] showed that the formation of phospham in the pyrolysis of pure $P_3N_3(NH_2)_6$ and $P_4N_4(NH_2)_8$ in an atmosphere of nitrogen occurs at ~ 300°C; this was shown by the loss in weight and the composition of the residue. The loss in weight was measured during the heating of phospham to 1000°C; however, the formation of phosphorus nitrides $(P_3N_5)_y$ and $(PN)_x$ was not observed, a difference from previous reports[203]. Often the material of the crucible in which the pyrolysis of the aminophosphazenes was carried out reacted with the reaction mixture[204]. The retention of the phosphazene ring in the formation of phospham from aminocyclophosphazenes is proved by the fact that the phospham obtained from $P_3N_3(NH_2)_6$ has a lower density than the product made from $P_4N_4(NH_2)_8$.[202]. The preparation of a foam based on phospham has also been described[205].

Deammonolysis has been used to obtain organo-substituted phosphams; thus polymers stable above 300°C were obtained by the pyrolysis of compounds of the general formula $P_3N_3R_x(NH_2)_{6-x}$, where R is an organic radical which can be fluorinated and $x \geqslant 3$.[206,207] Polymers with greater thermal stability were obtained by heating phenylaminocyclophosphazenes[208-210] above 300°C with a residual pressure of 10^{-3}–10^{-4} mmHg.

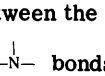
Organo-substituted phosphams were also synthesised by the reaction of chlorophosphazenes with amines. Aniline and HCP or OCP were used most frequently for this; in pyrolysis of the anilidocyclophosphazenes formed by the reaction of these substances aniline is released and phenylphosphams are formed[211]. The latter can again be converted into the original cyclic structures by heating with aniline which is impossible with unsubstituted phospham[202]. Phenylphospham is also formed on heating anilidochlorophosphazenes, obtainable in the non-polar replacement of chlorine in the initial chlorophosphazenes by aniline residues[212]. The formation of polymers from chlorophosphazenes and butylamine has also been reported[213].

Thermostable and fire-resistant polymers are obtained by the reaction of a mixture of crystalline chlorophosphazenes and acetaldehyde[102,214,215]. The process is accompanied by the liberation of HCl and CH_3COCl and, as has been shown[102], proceeds through the formation of cyclic products $(PNNC_6H_5)_n$ with their subsequent thermal polymerisation into a linear polymer. Similar polymers are formed in the reaction of chlorophosphazenes with diphenylurea and other amides[102]. It should be noted that an attempt to prepare the same polymers by ammonolysis of trichlorophosphazo-compounds $RN{=}PCl_3$ was unsuccessful[216]; instead polymers of the



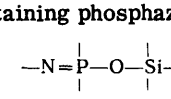
type were obtained; these decompose above 200°C with the formation of anilinium chloride.

The preparation of phosphazene polymers based on chlorophosphazenes and organic diamines has been described[164,217,218]. For this it is usual to employ a mixture of crystalline chlorophosphazenes in which some of the chlorine atoms can be replaced by inert organic radicals. But here the formation of cyclic spirane structures is also possible especially if the initial diamine contains an alkylene radical with 2–4 carbon atoms between the amino-groups[219-220].

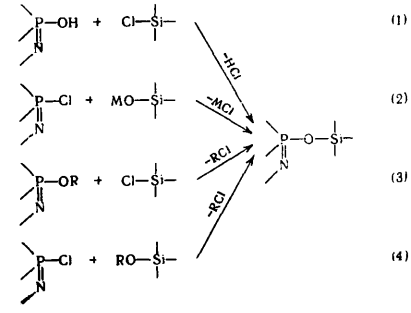
Water-soluble polymers with  bonds in the main chain are evidently also formed when linear chlorophosphazenes are treated with methanol and ammonia simultaneously[221,222].

3. Polyelementophosphazenes

In recent years there have been reports of the synthesis of heteropolyphosphazenes containing silicon, boron, germanium, and other elements. Many of the investigations relate to silicon-containing phosphazenes with



bonds in the main chain. There are four methods for making such polymers:



where M is an alkali metal or hydrogen, R = alkyl, and X is halogen.

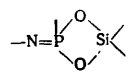
The first syntheses of silicon-containing polyphosphazenes by reaction (1) were effected in 1958–59. Dumont[223-225], who used the reaction of triphenyldihydroxychlorocyclotriphosphazotriene with diorganodichlorosilanes. The high thermal and hydrolytic stability of the polymers obtained was noted. Instead of the dihydroxyphosphazene derivative the tri-functional monomer $P_3N_3(OC_6H_5)_3(OH)_3$ can also be used[226]; this leads to the production of three-dimensional polymers or those capable of hardening.

To obtain siloxyphosphazene polymers of similar type by reaction (2), diphenylsilanediol and linear or cyclic chlorophosphazenes were used[227-229]. With the more reactive linear chlorophosphazenes the reaction takes place under milder conditions and leads to the formation of thermostable polymers[227], which can be used for preparing asbestosplastics[228]. However, in every instance the condensation of diphenylsilanediol with chlorophosphazenes is accompanied by side-reactions of homocondensation of dihydroxysilane and hydrolysis of chlorophosphazenes or of the semiproducts with water liberated in the condensation of dihydroxysilane. Therefore the polymers obtainable by reaction (2) contain a P–OH bond and also considerable amounts of water-soluble polymetaphosphimic acids[229]. The fraction of such side-reactions does not decrease on using acceptors (for example, quinoline). This is evidently due to the fact that the chlorophosphazene–tertiary amine systems are strong dehydrating agents[8].

It was therefore desirable to replace diphenylsilanediol by its siloxane, which is incapable of homocondensation, and thus exclude the appearance of water in the reaction mixture. However, it was shown[230] for monosiloxides and monosilanols that their reaction with hexachlorocyclotriphosphazotriene proceeds by scheme (2) but is considerably more complex and leads to the opening of the phosphazene ring and the formation of a mixture of low-molecular weight products, including disiloxanes. It was suggested that under certain conditions the polysiloxanes can react with the chlorophosphazenes with breaking of the Si–O–Si bond[230]. Thus, by heating hexaethyldisiloxane and HCP at 240°C in an ampoule for 6 h an oligomeric liquid and a solid insoluble polymer containing silicon and phosphorus were obtained[231].

A method for obtaining organosiloxyphosphazene polymers which is new in principle consists in the interaction of cyclic or linear alkoxyphosphazenes with organohalogenosilanes[232]. Its advantages are the high rate of reaction under comparatively mild conditions for carrying it out and the absence of side-reactions.

An investigation of the kinetics of this reaction in the case of hexabutoxycyclotriphosphazotriene and triorganohalogenosilanes[233] suggested that the process proceeds with heterolysis of the silicon–halogen bond and attack by the silicone cation at the oxygen atom of the alkoxyphosphazene. Under our conditions the formation of the organosiloxyphosphazene polymers on the basis of diphenyldichlorosilane and phenyltrichlorosilane[226] a marked decrease in the molecular weight of the polymeric products was noted owing to the partial formation of cyclic spirane structures of the type[226,234]:

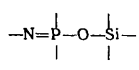


[226, 234].

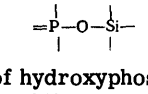
The formation of the latter can be prevented by starting from triphenoxytrialkoxycyclotriphosphazotrienes in which the phenoxy-groups do not react with chlorosilanes: it was then possible to obtain polymers which are three-dimensional or capable of subsequent hardening. Siloxyphosphazene polymers are also obtained by the reaction of cyclochlorophosphazenes with organoethoxysilanes[235].

It was found by differential thermal analysis and isothermal heating that the organosiloxyphosphazene polymers obtainable by reaction (3) start to decompose appreciably at 200°C as a result of the splitting off of the residual alkoxy-groups, whereas the thermal destruction of the main chain begins above 300°C.

Dumont's report[223,224] of the high hydrolytic stability of the phosphazene polymers with



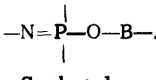
bonds was subsequently not confirmed. An investigation of the hydrolytic stability of the oligomeric and hardened organosiloxyphosphazene polymers showed that they are rather readily decomposed by water at the



bonds with formation of hydroxyphosphazenes and hydroxysilanes or the products of their homocondensation[226,234].

Silicon-containing phosphazene polymers of greater stability to hydrolysis can be obtained by the reaction of alkoxyphosphazenes with halogenoalkylsilanes[236].

Boron-containing phosphazene polymers of various types[237–239] and in particular with



bonds are interesting. Such polymers are obtained by the reaction of boric and organoboric acids with HCP and its alkoxy-derivatives[237] or by the condensation of boric acid (and other inorganic acids) with cyclic acids of alkoxyphosphazenes of the general formula

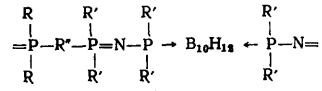
$$[PN(OR)_x(OH)_{2-x}]_n,$$

where $n = 3$ or 4 and $x \leqslant 2$.[238] On using the normal[237] and acid[238] alkoxyphosphazenes the proton-catalysed semiire-esterification of them by the boric and organoboric acids takes place accompanied by the loss of the corresponding alcohol.

In the direct reaction of HCP and boric acids the reaction takes place only in the presence of tertiary amines and leads to the formation in 50–70% yield of an infusible and insoluble polymeric product which is distinguished, according to differential thermal analysis, by high thermal stability (the loss in weight at 600°C is less than 20%) but by ready hydrolysis with boiling water.

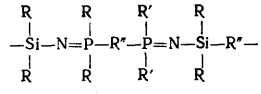
Hydrolytically stable boron-containing phosphazene polymers with a high softening point are obtained by the reaction of bis(azidodiarylphosphino)decaborane with such diphosphines as bis(diphenylphosphino)ethane, 1,4-bis(diphenylphosphino)benzene, etc.[239]

A process which can be effected by heating the initial substances in inert solvents and is accompanied by the liberation of nitrogen leads to the formation of polymers constructed from alternating units of the type



(where R and R′ are aryl and R″ is alkylene or arylene). Organoelemental polymers of the same type are synthesised by the reaction of the sodium derivative of decaborane with $P_3N_3Br_6$.[240]

The basis of a method for making an extensive class of heterochain element-containing phosphazene polymers is the reaction of phosphines with organoelemental azides[241]. In the reaction of the corresponding diphosphites and organoelemental diazides liquid phosphazene polymers of the type



are obtained, where R and R′ are alkyl or aryl and R″ is alkylene or arylene. These polymers are of interest as hydraulic liquids and lubricants or modifying additives for these materials[242–244].

4. Other Heteropolyphosphazenes

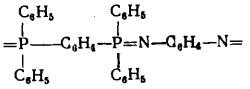
Many polyphosphazenes are known the macromolecules of which contain bonds different from those considered above. Thus resins analogous to the melaminoaldehydes are synthesised by the reaction of aminocyclophosphazenes and aldehydes at 60–80°C and pH 7–11.[245] Phosphazene-containing ureas and polyureas obtained by the reaction of aminocyclophosphazenes and aldehydes at 60°–80° and pH 7–11.[245] Phosphazene-containing ureas and polyureas are obtained by the reaction of $P_3N_3Cl_4(NH_2)_2$ with polyisocyanates[246]; however, this process is much more complex than the simple interaction of H_2N groups with isocyanato-groups[247]. $P_3N_3[N(CH_3)_2]_4(NH_2)_2$ is more reactive with isocyanates; this compound readily forms a urea derivative but in reaction with 2,4-toluene di-isocyanate in any ratio only two molecules of diaminocyclophosphazene are added to one molecule of di-isocyanate and products of higher molecular weight are not formed[247]. Urea derivatives can also be obtained from isocyanatocyclophosphazenes and amines[248]; when glycols are used phosphazene-containing polyurethanes are obtained[249].

Polyphosphazene products are also made by the reaction of HCP with guanidine urea, guanylurea, and other amides[250]. Phosphazene analogues of polycarbonates, formed in the phosgenation of hydroxycyclophosphazenes have been described[251] although the phosgenation products may have a more complex structure, since the reaction of

chlorocyclophosphazenes with organic acids and their salts leads to the breaking of the phosphazene rings[68].

Phosphazene polymers with P–O–P bonds in the main chain are obtained by heating a mixture of $P_3N_3R_4Cl_2$ and $P_3N_3R_4(OC_2H_5)_2$ (R = C_6H_5 or OC_6H_5); the process is accompanied by the release of ethyl chloride and the formation of thermostable products[252-254]. Polyphosphazenes with such bonds are formed in the heat treatment of alkoxyphosphazenes at 150–350°C [255] and also in the condensation of chlorocyclophosphazenes with alkyl phosphates, which is accompanied by the release of an alkyl halide and the formation of polymers stable to 500°C.[256]

A polymer with the structural units



and which softens at 150–200°C is obtained by the reaction of 1,4-bis(diphenylphosphino)benzene and 1,4-diazobenzene[257].

V. POLYMERS WITH PHOSPHAZENE GROUPS IN THE SIDE-CHAIN

Dishon[258] was the first to report the polymerisation of the allyl ester of cyclotriphosphazene into a viscous oil. Later[259] emulsions were obtained from unsaturated ethers of cyclophosphazenes. Infusible and insoluble polymers are formed in the polymerisation of dimethylamino- and phenylallyloxycyclotriphosphazatrienes in the presence of benzoyl peroxide[260]. In several studies it was found that triallyloxy-derivatives of phosphazenes are not polymerised at room temperature for 2 years and the ability to be sublimed in a vacuum up to 160°C is retained[261]. The polymerisation of butoxy- and phenoxy-allyloxycyclophosphazenes and also their copolymerisation with methyl methacrylate were investigated. The copolymers obtained did not exhibit high thermal stability[181]. Allyloxycyclophosphazenes and styrene were copolymerised at 70°C in the presence of benzoyl peroxide and the dinitrile of azoisobutyric acid. The determination of the copolymerisation constants allowed a conclusion to be drawn about the high activity of styrene; however, allyloxycyclophosphazene is more active than other allyl compounds[262]. Thermoplastic polymers and copolymers were obtained based on allylaminocyclophosphazenes. These polymers form stable films with good adhesion and, according to the thermogravimetric analysis, their loss in weight in air at 1000°C is 65%.[263,264]

VI. USES OF POLYPHOSPHAZENES

In contemporary literature, particularly patents and advertisements, there are two main trends in the practical use of phosphazene polymers: the use of homo- and hetero-polyphosphazenes as a basis for the preparation of stuffing plates [box? (Ed. of Translation)] coated with elastomers, etc., and the use of polyphosphazenes for modifying organic polymers and other materials to improve their thermal stability and fire resistance[265].

Use of polyphosphazenes as thermally stable and fire resistant materials. Comparatively long ago an attempt was made to use the thermal stability and fire resistance of polychlorophosphazene, by increasing its hydrolytic stability by replacing chlorine atoms by other atoms and groups. One of the variants of this exchange is based on the observed capability of polydichlorophosphazenes, during their formation in the thermal polymerisation of cyclochlorophosphazenes, to be bonded chemically with various silicate materials[266,267]. On this basis elastic electrical insulating coatings[268,269] and semiceramic products stable up to 500–600°C were prepared[270].

However, organophosphazene polymers are used most frequently for this purpose. The first attempts in this direction were made by Lipkin[101]. The products of the condensation of cyclochlorophosphazenes with polyhydroxyaromatic compounds have the greatest practical value[144-146,254]. Thus the polyhydroxyaryloxyphosphazenes obtainable by the method described in a patent[144] are recommended for use as adhesives, impregnating compositions, and prepared press articles. The same polymers which can be made in the presence of tertiary amines[146] are used as coatings on glass, ceramics, and metals; these coatings are distinguished by high shock resistance, resistance to solvents, acids, and alkalis. On hardening these polymers by heating at 244°C with 10% hexamethylenetetramine and a pressure of 176 kgf cm^{-2}; pressings are obtained with a tensile strength of 422, a bending strength of 703, and a compressive strength of 3160 kgf cm^{-2}.[145] Asbestoplastics from polyhydroxyaryleneoxyphosphazenes obtainable by a patented method[171] have a bending strength of 1600–1700 kgf cm^{-2} but after treatment at 500°C for 50 h it fell to no more than a half of this[271]. The same phosphazene binding agent is also used in making abrasive materials[272]. The products of the condensation of cyclochlorophosphazenes with polyhydroxyaromatic compounds, which are analogous in structure to phenolic resins but surpass them in thermal stability and also the products of the deammonolysis of phenyl(phenoxy)aminocyclophosphazenes[205-207] are undoubtedly some of the most promising phosphazene polymers in a practical respect.

Use of polyphosphazenes as modifiers of organic plastics. Additions of polyphosphazenes to organic polymers (phenolic, polyester, epoxy, and other resins) are made for the increasing the fire resistance and thermal stability of the latter. Polychlorophosphazenes[273-275] and the products of their amination or alcoholysis[276] are used for this purpose; for modification, polyphosphazenes with –OH, NH–, and other functional groups are more convenient to use. Thus, aminophosphazenes react readily with epoxy resins, forming modified products[277]. Fire-resistant polyurethane foams are obtained by using for the OH-containing component the products of the condensation of chlorocyclophosphazenes with glycols[188-191] and also by the introduction of polyphosphazenes with NHR groups into the mixture of components used for making polyurethanes[278].

Aziridinyl derivatives of polyphosphazenes are used as modifying hardeners for polyester compositions[279] and the products of the condensation of chlorocyclophosphanes and diphenols are modified with butadieneacrylonitrile copolymers[175]. Studies of the use of chlorophosphazene oligomers as catalysts for the polymerisation of organocyclosiloxanes have been described[280,281]. Copolymers of polychlorophosphazene with styrene and acrylonitrile have been obtained[282].

Alkoxypolyphosphazenes have been proposed for use as plasticisers for lacquers and cellulose films[122-123]. Polyphosphazenes of various types are widely used for conferring fire resistance on cellulose and other polymeric materials. Studies have been published[283-287] on the conferment of fire resistance on viscose silk, cotton, cotton fabrics, and on the improvement of the water and oil-resistance

of textile articles[288]. Hydroxymethylphosphazenes[285], water-soluble phosphams[289,290], condensation products of chlorophosphazenes with urea and chloroaniline[286], and the products from treating linear chlorophosphazenes with ammonia and methanol[222] are usually employed for this purpose. Polymethoxyphosphazenes[291] and lattices obtainable by the polymerisation of unsaturated bromo-containing alkoxycyclophosphazenes[259] are also used for improving the fire resistance of textiles.

Ion-exchange resins based on polychlorophosphazene[292], copolymers of unsaturated phosphazene derivatives with vinyl monomers[263,264], compositions based on phosphazene oligomers and polyacrylonitrile[293] and copolymers of acrylonitrile with HCP[294] have been synthesised.

Polychlorophosphazenes are used as activators for the hardening of polysiloxanes[295,296] and catalysts of the polymerisation of tetrahydrofuran[297]. Organo-substituted polyphosphazenes can be used for obtaining films, fibres, coatings, etc.[298]

Undoubtedly, in the near future many more possibilities for using polyphosphazenes of various types will appear; this is facilitated to no small extent by both the high thermal stability and other valuable properties of the polyphosphazenes and also their availability.

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Mendeleev Moscow
Chemical Technology
Institute

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New Contribution to the Development of Organoelementary and Organic Chemistry

R.Kh.Freidlina, M.I.Kabachnik, and V.V.Korshak

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I. INTRODUCTION

Twenty years ago, in a review of the achievements of the chemistry of organoelementary compounds, it was necessary to begin by defining the concept of "organoelementary chemistry", to formulate the region embraced by this science, and to specify its borderline position between organic and inorganic chemistry. Nowadays there is no need of this: organoelementary chemistry has become firmly established as a large and important branch of chemistry, covering a multiplicity of types of compounds, possessing numerous and well developed synthetic methods, specific reactions, and laws of reactivity, and having found diverse and important practical applications—from organoelementary medicinals, the industrial manufacture of which constitutes a typical example of fine organic synthesis, to organoelementary polymeric materials, combustion regulators, agricultural chemicals, and many other products of large-scale, so called heavy organic synthesis.

Organoelementary chemistry occupied a strong position in the development of general and theoretical aspects of chemistry, by providing extremely convenient materials for study by theoreticians and experimentalists. Not only in the USSR, which contains the first Institute of Organoelementary Compounds to be founded in the world, but also in other countries institutes and major laboratories appeared, specialising in the study of organoelementary chemistry, and publication of an international journal on the chemistry of organometallic compounds was started, while more than half the papers in the "Journal of General Chemistry" were devoted to organoelementary compounds.

An outstanding part in this birth and vigorous development of organoelementary chemistry as an independent branch of science was played by A. N. Nesmeyanov, in whose works and those of his many pupils organoelementary and especially organometallic chemistry found its greatest development. Ten years ago we gave in this journal a brief review of Nesmeyanov's scientific activities [1]. While referring readers to this review, in the present paper we shall concentrate our attention on the results of investigations made during recent years.

Nesmeyanov had an unusually broad range of scientific interests. He and his school undertook the leading fundamental researches in several fields of organometallic, organoelementary, and organic chemistry.

In spite of the diversity of subjects investigated by Nesmeyanov, they show a profound inner relationship in the logic with which the questions were posed and with which the investigation was developed. As example we may point to the logical and methodological connection existing between his diazo-method (1929) and his synthesis in 1955 of diarylchloronium salts, which greatly enriched one of the oldest branches of organic chemistry, that of chlorinated organic compounds. Just as at one time the diazo-method, originally proposed for synthesising organomercury compounds, was then developed by him in a comprehensive series of researches, leading to methods for the synthesis of organic compounds of several non-transition elements, so the "onium" synthesis was extended to the preparation of aromatic and heterocyclic diarylchloronium, diarylbromonium, triaryloxonium, sulphoxonium, and completely aromatic ammonium salts.

A profound inner connection exists between such apparently remote lines of research by Nesmeyanov as the investigation of β(and α)-substituted organometallic compounds (quasi-complex compounds), β-chlorovinyl ketones, and the tautomerism and dual reactivity of organic and organometallic compounds.

Using the popular definition of academics as romantics and classicists, we can say that Nesmeyanov is a romantic in the breadth of his interests and in his thirst for new discoveries, and a classicist in the accuracy of the expanded interests, the depth and comprehensiveness with which he works out problems.

During the past ten to fifteen years Nesmeyanov and his students have conducted researches in several completely new fields. Examples are the comprehensive and extraordinarily intensive investigation of organometallic compounds of transition metals, the discovery and investigation of the phenomenon of metallotropy, and the already mentioned investigations of onium and β-chlorovinyl compounds. He initiated and directed researches on synthetic foodstuffs, this work being reviewed in the present issue by V. M. Belikov, R. V. Golovnya, S. V. Rogozhin, G. L. Slonimskii, and B. V. Tolstoguzov.

A brief survey is given below of some new investigations by Nesmeyanov in the chemistry of organometallic compounds of transition and non-transition metals and on general aspects of organic chemistry.

II. ORGANOMETALLIC COMPOUNDS OF TRANSITION METALS

The past two decades have seen a vigorous growth of research on the organic compounds of transition metals. Not so very long—twenty years—ago it was considered that the transition metals did not form organometallic compounds. The few substances of this type then known, such as tetramethylplatinum, were regarded as a typical, exceptions to the rule. Nevertheless, an extremely characteristic feature of transition metals was the formation of numerous complex compounds of the Werner type, which had been widely studied in the chemistry of inorganic complexes and metal carbonyls, these forming a very peculiar, isolated "island" of chemical compounds marked off from the "continents" of inorganic and organic substances.

Fundamental changes have occurred in this field during recent years. Transition metals have been found to be capable of forming exceptionally numerous organometallic compounds of sandwich type, as well as π- and σ-complexes, which are sometimes extremely stable, as e.g. ferrocene, on the basis of which it has proved possible to construct new families of organic derivatives—not only metal–hydrocarbons but also halogeno-derivatives, alcohols, aldehydes, ketones, nitro- and amino-derivatives, carboxylic and organoelementary acids, and many others—a vast region of mixed structures, including sandwiches, π-complexes, and carbonyls, being found also between inorganic complex compounds and the new organic derivatives of transition metals. The carbonyl "island" has proved to form part of an immense new "mainland".

The chemistry of organic compounds of transition metals has proved exceptionally rich in new types of chemical bond, new laws, and new reactions. The Soviet school of organometallic chemists, with Nesmeyanov at its head, has made an exceptionally important contribution to the development of this field.

1. Metallocene and Arene Compounds of Iron (Ferrocene)

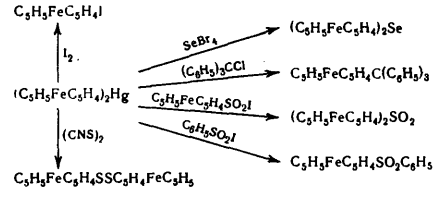
The main theme of this work was at first the development of the chemistry of ferrocene [2]. Nesmeyanov and his pupils have now carried out wide researches on the organic compounds of a large group of transition metals—iron, cobalt, manganese, rhenium, chromium, molybdenum, tungsten, vanadium, niobium, tantalum, titanium, zirconium, hafnium—and certain other elements.

In investigating ferrocene and its derivatives, Nesmeyanov and his coworkers solved a large group of general problems in this branch of chemistry. Examples are the determination of the reactivity of ferrocene compounds as non-benzenoid aromatic systems, the establishment of specific differences in the reactivity of ferrocene and aromatic benzenoid compounds, rules of orientation in substitution reactions in ferrocene and its derivatives, the magnitude of polar effects in the reactions of ferrocene compounds, the polar characteristics of the ferrocenyl group as a substituent, the effect of ferrocenyl on the stability of adjacent cationic, radical, and anionic centres, electronic effects in the ferrocene series, the development of methods for demonstrating the structure of ferrocene derivatives, and the transition from ferrocene to compounds of other types. The list of problems can easily be extended.

In the solution of these problems Nesmeyanov made wide use of the whole available range of chemical, physical, and physicochemical methods of investigation. Only a brief survey of some of the results obtained can, of course, be given in this paper.

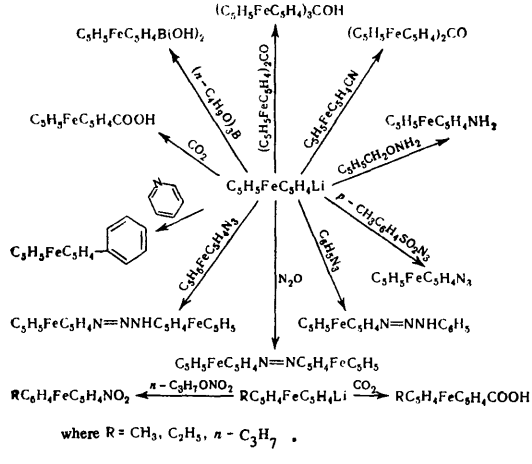
In order to solve the problems it was first necessary to develop synthetic methods for, and examine the chemical reactions of, various derivatives of ferrocene. At the start of this series of investigations only a single substitution in the cyclopentadienyl ring of ferrocene was known, this being the reaction with acid halides and anhydrides to form ketones [3]. Since the classical electrophilic substitution reactions—halogenation, nitration, sulphonation, etc.—are difficult in the ferrocene series (because of the ease of oxidation of ferrocene), Fischer and Jira [4] spoke against an analogy between ferrocene and aromatic compounds.

Scheme 1



In the very first paper of this series, Nesmeyanov and his coworkers [5] showed this view to be incorrect, by effecting the mercuration of ferrocene with mercury acetate and its metallation with butyl-lithium. Mercury and lithium derivatives of ferrocene have since been widely used in the preparation of other ferrocene compounds (Scheme 1). In particular it has proved possible for the first time, with mercury derivatives of ferrocene as starting material, to obtain halogenated derivatives [6], and ferrocenylamine from ferrocenyl-lithium [7] (Scheme 2).

Scheme 2



The lithium compounds can be converted into carboxylic and boronic acids, ketones, alcohols, amines, azides, and nitro-, azo-, and diazamino-derivatives of the ferrocene series (Scheme 2).

The direct alkylation of ferrocene [8,9] by alkyl halides and alkenes in the presence of aluminium chloride was accomplished by Nesmeyanov and Kochetkova during 1956–1958. Introduction of the first alkyl group into the ferrocene molecule favours further alkylation. Nesmeyanov et al. have since shown by gas–liquid chromatography that

all possible isomeric di- and tri-alkylated ferrocenes are thus formed [10-12]. Use of a mixture of anhydrous aluminium chloride and lithium tetrahydroaluminate increases the yield so greatly that alkylation becomes a method for preparing certain homologues of ferrocene.

Study of the absorption spectra of monoalkylated and heteroannular dialkylated ferrocenes and comparison with those of the corresponding acyl derivatives have permitted an assignment of the absorption bands of ferrocene itself [10-12]. The agreement of the change in the spectra predicted theoretically (by calculation based on the molecular orbital method to the Hückel approximation) on passing from ferrocene to its substituted derivatives with the experimental data has confirmed the correctness of this assignment [13].

Investigation of the nuclear magnetic resonance spectra of homologues of ferrocene containing primary, secondary, and tertiary alkyl groups indicates hyperconjugation of the alkyl substituent with a cyclopentadienyl ring of the ferrocene system [14].

Nesmeyanov and his students have discovered many new reactions—acylation [15,16], sulphonation [17], phosphorylation [18]—of electrophilic substitution. Together with Kursanov, Setkina, and their coworkers a study was made of the deuteriation of ferrocene and its substituted derivatives [19-23]. Investigations have been made of the nucleophilic substitution of halogen in ferrocenyl halides [24-26], of radical substitution—arylation by aromatic diazo-compounds [5,7,27]—and many other reactions [2,28], e.g. the condensation of ferrocene with aldehydes [29].

o-Carboxybenzoylferrocene undergoes reactions of a peculiar type [30-33]. By ring–chain tautomerisation in its cyclic form it exhibits several reactions of the α-ferrocenylcarbonium ion, e.g. extremely readily occurring nucleophilic substitutions initiated by acids. The ferrocene analogue of anthraquinone—"ferrocoanthraquinone"—has been obtained by a series of transformations of the "open" acyclic form of *o*-carboxybenzoylferrocene.

Nesmeyanov, Vil'chevskaya, Kochetkova, and their coworkers accomplished the phosphorylation of ferrocene with phosphorus trichloride, obtaining triferrocenylphosphine oxide. This reaction has considerable value for alkyl, aralkyl, and aryl derivatives of ferrocene. The peculiar behaviour of these compounds towards nucleophilic and electrophilic reagents distinguishes them from the corresponding aromatic and aliphatic organophosphorus compounds [34,35].

The investigation by Nesmeyanov, Sazonova, and Drozd of ferrocenylboronic acids has proved extremely fruitful for synthetic purposes [36-40]. In particular, monochloro- and 1,1′-dichloro-ferrocene were obtained for the first time by replacement of the $B(OH)_2$ group in these acids, and hydroxy- and amino-ferrocenes have been prepared by the same method (Scheme 3).

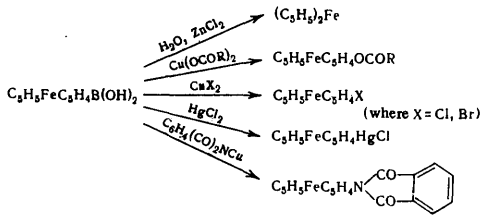
The synthesis of chlorinated ferrocenes made it possible to obtain various compounds by a nucleophilic substitution of the chlorine by other groups. It was shown [24,25,41,42] that the halogen in halogenated ferrocenes is easily exchanged in the presence of copper salts; amino- and hydroxy-derivatives of ferrocene, as well as azides, nitriles, and other derivatives, have been obtained in this way (Scheme 4).

Without attempting to exhaust all the methods of preparing ferrocene compounds developed by Nesmeyanov and his students, we may mention a series of papers on preparations involving the use of *NNN*-trialkylammonium derivatives of ferrocene (Scheme 5) (together with Perevalova, Shilovtseva, Ustynyuk, et al. [43-48])

A specific "ricochet" substitution (cyanation) involving iron has been discovered [49-51]. Ferricinium salts (or ferrocene in the presence of aluminium chloride) on treatment with hydrocyanic acid yield ferrocenecarbonitrile:

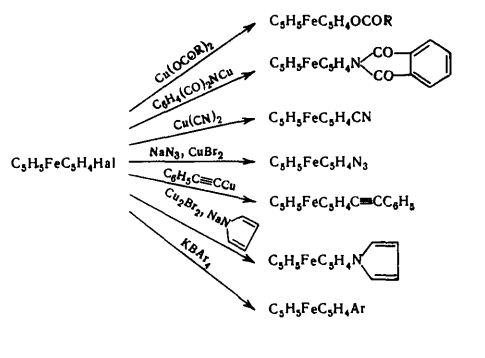
$$(C_5H_5)_2Fe \xrightarrow[FeCl_3]{HCN} C_5H_5FeC_5H_4CN\ .$$

Scheme 3

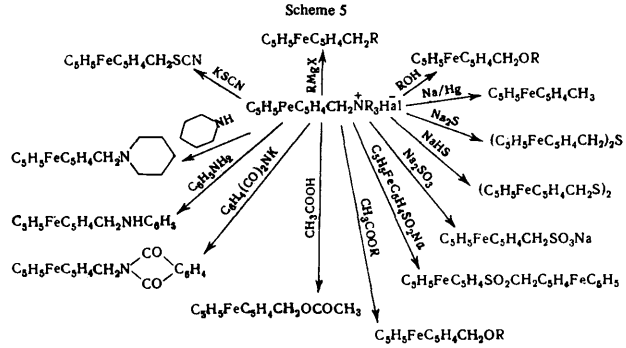


This is not a bimolecular nucleophilic substitution, since it does not obey the rules of orientation for nucleophilic substitution. Thus electron-acceptor substituents (*p*-nitrophenyl, phenylsulphonyl, acetyl, and chloro-, bromo-, cyano-, and nitro-groups) make cyanation more difficult and favour the formation of heteroannular isomers [50]. The cyanide anion probably first attacks the iron atom of the ferricinium cation with liberation of the proton from the hydrocyanic acid molecule (the pH of the medium decreases). The cyano-group then migrates into the five-membered ring with simultaneous reduction of the iron.

Scheme 4



Scheme 5



Representatives of the principal types of compounds of the ferrocene series have been obtained by the above reactions and several others, in most cases the mechanism of

their formation (electrophilic, nucleophilic, radical substitution) has been established, and their chemical properties have been studied.

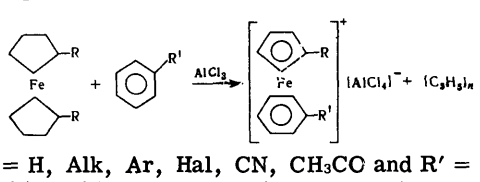
The reactions of many functional derivatives of ferrocene are analogous to those of the corresponding aromatic compounds. Several fundamental differences in chemical reactivity have been observed between ferrocene compounds and their aromatic analogues. Thus the former are incapable of the typical rearrangements of aromatic compounds: azoferrocene, for example, cannot undergo the benzidine rearrangement[52], and the allyl ether of ferrocenol is unable to rearrange into allylferrocenol[53]. This is explained by the inability of the ferrocene ring system to transmit *T*-effects requiring quinoid transition states.

A series of papers by Nesmeyanov, Gubin, and Perevalova has been devoted to electronic effects in ferrocene compounds[54–57]. The formal oxidation potentials of a large number of derivatives of ferrocene[54,55], the dissociation constants of acids and phenols, and the basic dissociation constants of amines of the ferrocene series[56] have been determined, and the infrared and ultraviolet spectra of several substituted ferrocenes studied. The application of correlation equations to an analysis of the results revealed the difference between the interaction of substituents with the phenyl and with the ferrocenyl ring systems, and enabled ferrocenyl to be characterised as a substituent[57].

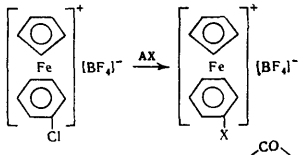
Both in the ferrocene system and in the benzene ring a ferrocenyl substituent exhibits electron-donor properties, the effect of the ferrocenyl being determined by the combination of a strong positive inductive effect with a fairly weak positive conjugative effect.

The effect of ferrocenyl on the stability of a neighbouring cationic centre is consistent with the above description of ferrocenyl as a substituent: it stabilises a neighbouring carbonium centre, carbonium salts containing ferrocenyl residues in the α-position being extremely stable[58,59]. The triferrocenylmethyl cation is also stable at room temperature[60].

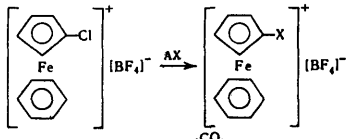
A remarkable type of ligand exchange was discovered in ferrocene by Nesmeyanov and Vol'kenau[61,62]. When ferrocene interacts with benzene and its derivatives in the presence of aluminium chloride, one five-membered ring is exchanged for an arene ring with the formation of arenecyclopentadienyl derivatives of iron:



where R = H, Alk, Ar, Hal, CN, CH_3CO and R′ = H, Alk, Ar, Hal, OAlk, OAr, CH_3, CH_3CONH. The effect on this reaction of substituent groups both in the ferrocene and in the arene has been investigated. The reactivity of the arenecyclopentadienyl compounds of iron thus made available has been studied. In particular, the replacement of halogen in the five-membered and six-membered rings by other groups has been investigated:



where X = OAlk, OAr, SAr, SAlk, C_6H_4(CO)(CO)N, NH_2, NHK, $C_5H_{10}N$; A = Na, K, H



where X = OAlk, C_6H_5S, C_6H_4(CO)(CO)N, NH_2, NHC_6H_{11}, $C_5H_{10}N$.
A = Na, K, H

2. Carbonyls and Organometallic Derivatives of Metal Carbonyls

In a long series of papers Nesmeyanov, Anisimov, Kolobova, Makarov, Pasynskii, and Ioganson have elaborated methods for the synthesis of organometallic compounds of manganese, rhenium, niobium, tantalum, vanadium, and several other transition metals, and have studied their chemical reactions, physicochemical properties, comparative reactivity, the nature of the bond, the mutual influence of groups, and many other aspects of their chemistry[63,64].

Mixed compounds have been investigated, in which the metal is bound to cyclopentadienyl and carbonyl groups, as well as aromatic derivatives of manganese and rhenium carbonyls containing a metal–carbon σ-bond, and polymetallic derivatives of molybdenum and tungsten carbonyls containing a direct metal–metal bond with elements of Group IVb.

A method has been developed for the synthesis of cyclopentadienyl derivatives of carbonyls of metals in Group VII:[63,64]

$$C_5H_5Na + ClM(CO)_5 \rightarrow C_5H_5M(CO)_3 + 2CO + NaCl$$

where M = Mn, Re.

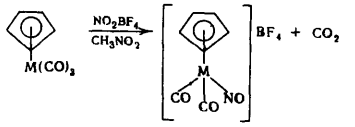
The acylation[65], mercuration[65], chloromethylation[65], phosphorylation[65], and deuteriation of tricarbonylcyclopentadienylmanganese (TCCM) and to some extent of its homologues[66–68] have been accomplished, as well as the deuteriation[66–68], sulphonation[69], and mercuration[69] of tricarbonylcyclopentadienylrhenium (TCCR). The cyclopentadienyl derivatives of Group VII metals have been shown to resemble ferrocene in possessing aromatic properties, the above rhenium compound being less active in electrophilic substitutions, but more active in protophilic substitutions, than is the corresponding manganese derivative.

It has been discovered[70,71] that the ring in TCCM and TCCR can be metallated.

The transformations of the lithium, mercury, and chloroderivatives of TCCM and TCCR have been studied[70,71]. Methods have been worked out for synthesising various compounds containing in the cyclopentadiene ring such groups as COOH, NH_2, $B(OH)_2$, HgCl, Cl, Br, RCO, and many others. These reactions are set out in Scheme 6.

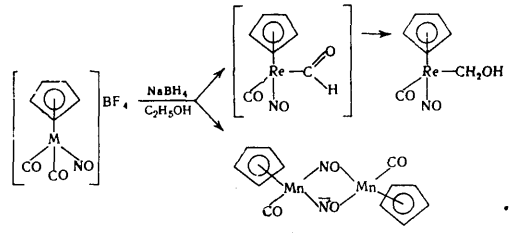
The chloromethylation of TCCM and the chemical reactions of the chloromethyl derivatives have been studied[65].

TCCM and TCCR react in very peculiar fashion with nitryl tetrafluoroborate. Instead of the expected nitration of the ring the reaction involves simultaneous oxidation–reduction and ligand exchange with the formation of nitrosyl complexes:

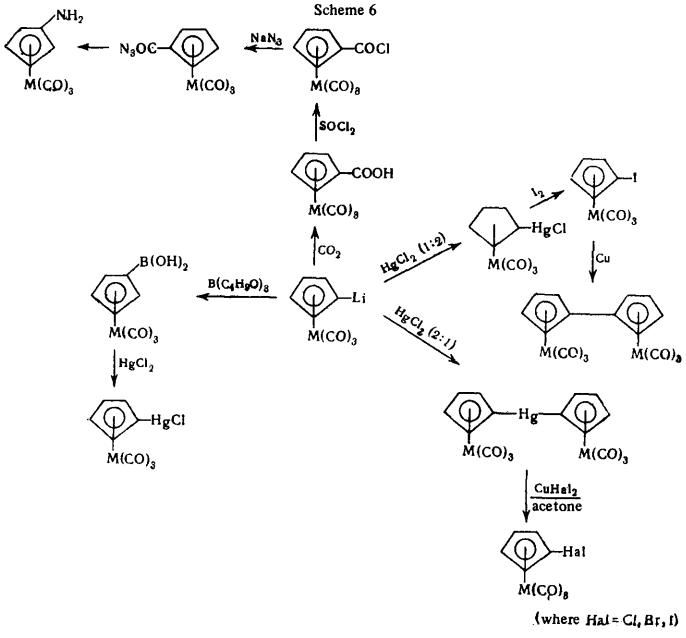


(where M = Mn, Re)

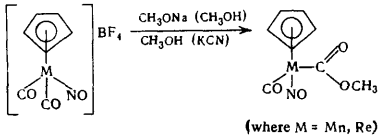
Several differences in chemical behaviour have been established between the cyclopentadienyl–carbonyl complexes of manganese and of rhenium. When the fluoroborate complexes are reduced with sodium tetrahydroborate in ethanol, the manganese derivative yields a dimeric product, but the rhenium analogue gives an alcohol:



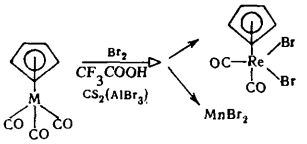
Scheme 6



The action on the fluoroborate complexes of a sodium alkoxide in methanol, or of methanol in the presence of potassium cyanide, results in esters (reaction at the carbonyl group):

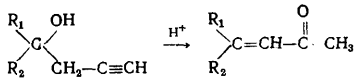


Bromination under conditions of electrophilic substitution goes in different ways with TCCR and TCCM:



The chemical behaviour of ketones of TCCM has been investigated. Reduction of the ketones [72], hydration of the carbonyls, and interaction of the former with Grignard and Iotsich reagents have been accomplished, and the rearrangement of tertiary α-acetylenic alcohols has been studied [73,74].

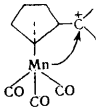
The rearrangement of β-acetylenic alcohols has been discovered [75]:



where R_1 = TCCM, $C_5H_4FeC_5H_5$ and R_2 = CH_3, C_2H_5, C_6H_5.

Ketones of TCCM on treatment with bromine yield α-bromoketones [76]. A study has been made of the mobility of halogen in the α-position with respect to the carbonyl group in nucleophilic substitutions and condensations.

The TCCM residue is more efficient than phenyl in stabilising an adjacent carbonium centre. Yet it also surpasses phenyl in reactions involving a neighbouring α-anionic centre. Thus a TCCM residue possesses stronger negative and positive mesomeric effects than does phenyl. Its stronger positive mesomeric effect (+M) is obviously due to the part played by the electronic environment of manganese in stabilising the α-carbonium centre:



Investigation of TCCM, TCCR, and their derivatives by physical methods (infrared, nuclear magnetic resonance, nuclear quadrupole resonance spectra, etc.) has enabled differences in the fine structure of the manganese and rhenium compounds to be formulated (relative electron density of the cyclopentadienyl rings, order of the metal–carbonyl bond, etc.).

The reactions of the carbonyl–cyclopentadienyl complexes of vanadium, niobium, and tantalum with p- and π-donor ligands have been examined [77], and new types of complexes of these metals obtained containing cyclopentadienyl, carbonyl, and substituted acetylenic groups. For example, products of the successive incorporation of one, two, and three diphenylacetylene molecules with one niobium atom have been isolated, the final product being hexaphenylbenzene. This process can be regarded as a model of the trimerisation of acetylenic hydrocarbons on complexes of transition metals.

Methods have been worked out for preparing derivatives of manganese and rhenium carbonyls containing metal–carbon σ-bonds [78], of the types $XC_6H_4COM(CO)_5$ and $XC_6H_4M(CO)_5$, where X is a substituent in the aromatic ring. The way in which the electronic effect of the substituent X in these compounds is transmitted via the metal atom to the carbonyl groups has been examined by various physical methods [79].

3. Heteropolymetallic Derivatives of Metal Carbonyls

It is well known that, unlike π-complexes of transition metals, the organic σ-derivatives are unstable if they contain no other stabilising ligands. When ligands (CO, π-C_5H_5, etc.) capable of accepting electron density from the metal into vacant π-orbitals are introduced into the coordination sphere of the metal atom, the metal–carbon σ-bond is considerably stabilised. The preparation of several stable organic σ-derivatives of metal carbonyls has opened up the possibility of synthesising stable compounds containing σ-bonds between atoms of transition metals and of elements in Group IVb other than carbon.

The researches of Nesmeyanov and his students showed that compounds containing covalent bonds between atoms of

transition metals and of Group IVb elements can be obtained by several methods—(1) exchange interaction of salts of metal carbonyls with organic halides of silicon, germanium, tin, or lead [80-93], e.g.

$$R_3MX + NaRe(CO)_5 \rightarrow R_3MRe(CO)_5$$
$$R_2MX_2 + 2NaMo(CO)_3C_5H_5 \rightarrow R_2M[Mo(CO)_3C_5H_5]_2$$
$$RMX_3 + 3NaCo(CO)_4 \rightarrow RM[Co(CO)_4]_3$$
$$SnX_4 + 4NaFe(CO)_2C_5H_5 \rightarrow Sn[Fe(CO)_2C_5H_5]_4$$

where M = Si, Ge, Sn, Pb, R = Alk, Ar, and X = Cl, Br.

(2) Reactions involving "insertion" of germanium dichloride at metal–halogen bonds [84]:

$$Cl-Fe(CO)_2C_5H_5 + GeCl_2 \xrightarrow{\text{dioxan}} Cl_3Ge-Fe(CO)_2C_5H_5$$
$$Cl-M'(CO)_3C_5H_5 + GeCl_2 \rightarrow Cl_3Ge-M'(CO)_3C_5H_5$$

where M′ = Mo, W; or at a metal–carbon bond:

$$R-Fe(CO)_2C_5H_5 + GeCl_2 \xrightarrow{\text{dioxan}} RCl_2Ge-Fe(CO)_2C_5H_5$$

where R = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, $C_6H_5CH_2$. It is also possible for germanium dichloride to be inserted into metal–metal bonds under mild conditions:

$$C_6H_5(OC)_2Fe_2 + GeCl_2 \xrightarrow[\text{dioxan}]{} Cl_2Ge[Fe(CO_2)C_5H_5]_2 .$$

Insertions of tin dihalides into dinuclear carbonyls in which the two parts are linked by a direct metal–metal bond, e.g. $[C_6H_5(CO)_3M']_2$ (M′ = Mo, W) or $M'_2(CO)_{10}$(M′ = Mn, Re), takes place at high temperatures or on ultraviolet irradiation:

$$M'_2(CO)_{10} + SnCl_2 \rightarrow Cl_2Sn[M'(CO)_5]_2$$
$$[C_5H_5(CO)_3M']_2 + SnCl_2 \rightarrow Cl_2Sn[M'(CO)_3C_5H_5]_2 .$$

With molybdenum and tungsten derivatives, compounds containing one metal–carbonyl group, such as $Cl_3SnM'(CO)_3C_5H_5$, have been isolated together with the above insertion products.

(3) Trichlorogermyl derivatives of the carbonyls of molybdenum, tungsten, iron, and manganese have been obtained by reaction between trichlorogermane and the corresponding carbonyl halides [85,86]:

$$ClMn(CO)_5 + Cl_3GeH \rightarrow Cl_3GeMn(CO)_5 + HCl .$$

(4) Compounds containing bonds between cobalt and a Group IVb element have been prepared also directly from octacarbonyldicobalt and organic halides of germanium, tin, or lead [87]:

$$R_nMX_{4-n} + Co_2(CO)_8 \rightarrow R_nX_nM[Co(CO)_4]_{4-m-n}$$

where R = Alk, Ar, n = 1–3, m = 2–0, and M = Ge, Sn, Pb. The number of carbonylcobalt groups linked directly to the atom of the non-transition element is determined by the ratio of the reactants, but does not exceed three.

The methods enumerated above have been used to obtain many new compounds containing atoms of Group IVb elements together with 1–6 identical or differing atoms of transition metals.

Derivatives, containing a metal–metal σ-bond, of Group IVb elements and metal carbonyls are mostly crystalline substances, soluble in the usual organic solvents, and insoluble in water. A considerable proportion of them are coloured, varying from pale yellow to red.

In the solid state compounds containing metal–metal bonds (with the exception of certain derivatives of cobalt) are stable to the action of oxygen and atmospheric moisture. Depending on the nature of the transition metal the thermal and oxidative stability of the complexes increases in the sequence

$$Co < Cr < Mo < W < Mn < Re < Fe .$$

The most stable compounds are those containing a tin–transition metal bond. Derivatives containing germanium and especially lead atoms are less stable. Among compounds containing transition metal–silicon bonds derivatives of carbonyls of Group VII metals (manganese, rhenium) are the most stable, withstanding prolonged heating (at 160–170°C for 35 h) without appreciable decomposition. As the number of carbonylmetal groups combined with the non-transition metals increases, the thermal and oxidative stability diminishes. Derivatives containing three or four metal atoms, of the types $R_2M[M'(CO)_mL]_2$ and $RM[M'(CO)_mL]_3$, are the least stable. Tetrametallic derivatives have been obtained mainly with tin and silicon.

The chemical properties of compounds containing metal–metal bonds with two or more metal-bound fragments depend in considerable measure on the nature of the stabilising ligands, the electronegativity of the substituents combined with the non-transition metals, and several other factors.

Three types of reaction—at metal–metal, metal–carbon, and metal–carbonyl group bonds—are possible with compounds of the given type, containing R–M–M′–CO bonds, where R = Alk, Ar, Hal. The action of halogens, halogen hydrides, hydrohalic acids, and several other reagents has been investigated.

The reactions of derivatives containing two metal atoms are specific, depending on the conditions, the nature of the transition metal, and the ligands attached to it.

The action of chlorine or bromine on tin derivatives of manganese and rhenium carbonyls at temperatures from 0° to 70°C is accompanied by cleavage of carbon–tin bonds, while the metal–metal bonds are preserved. The replacement of phenyl groups may be successive:

$$(C_6H_5)_2Sn[M'(CO)_5]_2 \xrightarrow{+2Hal_2} C_6H_5Hal_2Sn-M'(CO)_5 \rightarrow Hal_3Sn-M'(CO)_5$$

where M′ = Mn, Re and Hal = Cl, Br.

In cobalt-containing complexes a metal–metal bond always undergoes cleavage on treatment with halogens under any conditions.

Germyl derivatives of Group VII metal carbonyls do not react with halogen hydrides, whereas the stannyl derivatives do interact with them, the carbon–tin bonds being cleaved while the metal–metal bonds are maintained. The replacement of phenyl groups may be partial or complete depending on the reaction conditions. The above reactions of the dimetallic derivatives are analogous to those of classical organotin compounds.

Reactions between trimetallic complexes and hydrogen halides also involve replacement of phenyl groups and preservation of metal–metal bonds, e.g.

$$(C_6H_5)_2Sn[Mn(CO)_5]_2 \xrightarrow{+2HCl} Cl_2Sn[Mn(CO)_5]_2 .$$

A metal–metal bond is considerably stabilised by the presence of electronegative substituents attached to the non-transition metal. Thus the interaction of $(C_6H_5)_3SnFe(CO)_2C_5H_5$ with mercuric chloride is accompanied by cleavage of the tin–iron bond, whereas the corresponding chloro-derivative does not react:

$$(C_6H_5)_3SnFe(CO)_2C_5H_5 + HgCl_2 \rightarrow (C_6H_5)_3SnCl + ClHgFe(CO)_2C_5H_5 .$$

On interaction with nucleophilic agents, halogen-containing germyl and stannyl derivatives of metal carbonyls, like

ordinary organometallic halides of Group IV elements, exchange halogens for the corresponding anions to form derivatives having different functional substituents attached to the non-transition metal atom, the metal–metal bonds being preserved [88–90]:

$$[L(CO)_mM']_2MCl_2 + 2R^- \rightarrow [L(CO)_mM']_2MR_2$$

where R = NO_2, NO_3, C_2H_3S, C_5H_5, NCS, etc.

From these reactions it has been possible to ascertain the behaviour of metal–metal bonds in these complexes towards various nucleophilic reagents and different reaction media, and to prepare several derivatives containing donor or acceptor substituents attached to the non-transition metal atom. Under these conditions the stannyl derivatives of carbonyls of Groups VII and VIII metals have proved to be the most stable. Derivatives of Group VI metals readily break down in alkaline media. On the other hand, derivatives of iron carbonyl show exceptional stability towards both acidic and alkaline reagents. Derivatives of manganese and rhenium carbonyls occupy an intermediate position, the former being the less stable. Derivatives of cobalt carbonyl are the most sensitive to conditions in the exchange reactions.

The germyl and stannyl derivatives of manganese, rhenium, and iron react with Grignard reagents in the normal fashion:

$$Br_3GeMn(CO)_5 + 3C_6H_5MgBr \rightarrow (C_6H_5)_3GeMn(CO)_5$$

$$[C_5H_5(CO)_2Fe]_2MCl_2 + 2RMgX \rightarrow [C_5H_5(CO)_2Fe]_2MR_2$$

where R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_5 and M = Ge, Sn.

The carbonylmetal portions of dinuclear and polynuclear derivatives exhibit all the properties characteristic of ordinary metal carbonyls: they are able to exchange the carbonyl groups for other ligands, e.g. triphenyl-phosphine, -arsine, and -stibine, without cleavage of metal–metal bonds:

$$R_3SnM'(CO)_5 + P(C_6H_5)_3 \rightarrow R_3Sn{-}M'(CO)_4P(C_6H_5)_3 .$$

Investigation of these reactions has shown that the ease of exchange is largely governed by the electronegativity of the substituents attached to the non-transition metal atom. The presence of electron-acceptor substituents facilitates exchange; electron-donor substituents, on the other hand, make exchange more difficult.

Derivatives containing two metal atoms undergo extremely interesting photochemical reactions with π-donor ligands. Thus the ultraviolet irradiation of $(C_6H_5)_3Sn{-}Fe(CO)_2C_5H_5$ in the presence of ethylene at atmospheric pressure results in the detachment of one carbonyl group with the formation of a π-ethylene complex:

$$(C_6H_5)_3Sn{-}Fe(CO)_2C_5H_5 + CH_2{=}CH_2 \xrightarrow[\text{benzene}]{h\nu} (C_6H_5)_3Sn{-}Fe(CO)(CH_2{=}CH_2)C_5H_5 + CO .$$

An X-ray study of the crystalline structure of compounds [91] containing tin–iron, tin–manganese, and tin–cobalt bonds has shown that the metal–metal bonds are always shorter than the sums of the singly bound covalent radii of the metals and are very sensitive to the nature of substituents attached to the Group IVb atom. Thus in compounds of the type $X_2Sn[Fe(CO)_2C_5H_5]_2$ increase in the electronegativity of X is accompanied by an appreciable shortening of the tin–iron bonds together with an increase in the iron–tin–iron angles (see Table).

In the same series of compounds there is observed a parallel increase in the frequency νCO, which indicates an increase in the carbon–oxygen bond order:

$$X{-}Sn{-}M{=}C{=}O \leftrightarrow \bar{X}{-}Sn{-}M{-}C{\equiv}\overset{+}{O} .$$

Compound	Bond lengths, Å			Fe–Sn–Fe angle, °	ν_{CO}, cm^{-1}	$\sigma_{C_5H_5}$,* p.p.m.
	Sn–Fe	Fe–CO	C–O			
$(CH_3)_2Sn[Fe(CO)_2C_5H_5]_2$	2.60	1.72	1.20	124	1981	4.91
$(ONO)_2Sn[Fe(CO)_2C_5H_5]_2$	2.56	1.72	1.19	126	2027	4.93
$Cl_2Sn[Fe(CO)_2C_5H_5]_2$	2.49	1.76	1.08	128.6	2022	5.19

*These are apparently τ-values (Ed. of Translation).

All these changes have been explained by the hypothesis of d_π–d_π interaction between completed *d*-orbitals of the transition metal and vacant *d*-orbitals of the tin atom, with a consequent increase in order of the tin–iron bond. Further support for the occurrence of such interaction has been obtained from an analysis of the infrared spectra [79], the most convenient for investigation being those of manganese carbonyl derivatives of the type $X_3MMn(CO)_5$. These compounds have an approximately octahedral structure, with a substituent other than carbonyl at one of the vertices of the octahedron. The presence of two types of carbonyl groups (equatorial and axial) in these molecules enables us to delimit the transmission of electronic effects of MX_3 substituents through the metal atom to the carbonyl groups.

Analysis of the infrared spectra reveals that the frequency of the vibrational band due to equatorial carbonyl groups varies linearly with the Taft inductive σ^*-parameter for the MX_3 groups, whereas the vibrational frequency of the axial group is influenced by both inductive and mesomeric effects of the substituent.

All compounds containing a bond between a manganese atom and a non-transition element of Group IVb exhibit a considerable contribution of d_π–d_π interaction to the metal–metal bond.

The infrared spectra of π-cyclopentadienyl derivatives of the carbonyls of molybdenum, tungsten [92], and iron [93] containing M–Ge or M–Sn bonds, of the types $[C_5H_5(CO)_3M']_2MX_2$ and $[C_5H_5(CO)_2Fe]_2MX_2$, exhibit satisfactory correlation between the frequencies νCO and the σ^*-values for the substituents X, which indicates a predominantly inductive transfer of electronic effects from substituents of the non-transition metal to carbonyl groups located at an angle to the metal–metal bond.

In a study of the infrared spectra of compounds of the type $X_2M[Fe(CO)_2C_5H_5]_2$, where M = Ge or Sn, it has been suggested that rotational isomers of these compounds are present in solutions, as a consequence of rotation about the germanium–iron or tin–iron bonds [94]. Analogous isomers are possible also with molecules containing one metal–metal bond, in which several different substituents are attached to the non-transition metal atom. This hypothesis has been confirmed for the compound $CH_3Cl_2GeFe(CO)_2C_5H_5$ by determining the relative intensities of the νCO bands in the infrared spectra in various solvents and at various temperatures.

4. Organometallic Compounds of Titanium, Zirconium, and Hafnium

Nesmeyanov, Nogina, and their coworkers have investigated cyclopentadienyl derivatives of titanium, which exhibit several fundamental differences from ferrocene and its derivatives. They have established that cyclopentadienyl compounds of titanium readily decompose under the action of nucleophilic reagents [95-97]. In several cases, for example $C_5H_5Ti(OC_2H_5)_3$ and $(C_5H_5)_2Ti(OCOCH_3)_2$, the Ti–C_5H_5 bond is cleaved even by treatment with ethanol at 20°C. Furthermore, mono- and di-cyclopentadienyl derivatives of quadrivalent titanium, unlike ferrocene, undergo no substitution reactions (acylation, alkylation, mercuration, cyanation, and probably radical substitution reactions). In this connection Nesmeyanov concerned himself mainly, in the chemistry of the cyclopentadienyl derivatives of titanium, with the exchange of ligands on the titanium and the accompanying change in the properties of the Ti–C_5H_5 bond. Several convenient and accessible methods were developed for preparing various types of mono- and di-cyclopentadienyl derivatives of titanium [98-101]. Examples are methods for synthesising trialkoxides, trihalides, and also cyclopentadienyl derivatives of titanium which are at the same time inner-complex compounds, as well as compounds containing different atomic groupings (alkoxy-, aryloxy-, and acyloxy-groups, halogen atoms, and several others) attached simultaneously to the titanium atom.

Chemical and physical methods have been used to investigate the way in which the effect of various ligands is transmitted through the titanium atom to the cyclopentadienyl ring [102-104]. It was found that, as the number of electron-acceptor halogen atoms in the molecule decreases, the yield of cyclopentadiene produced by the alcoholysis and hydrolysis of the above substances increases, as also the yield of ferrocene on reaction with the iron(II) ion [102-104]. This chemical behaviour, combined with the results of comprehensive physical investigations of these compounds by infrared, mass, and nuclear magnetic resonance spectroscopy and conductivity measurements on several substances, has led to the conclusion that the bond between titanium and the cyclopentadienyl ring becomes more polar as the electron-acceptor properties of the ligands diminish [102-104].

The nature of the ligands combined with the titanium affects also the type of rotation of the cyclopentadienyl rings in its dicyclopentadienyl derivatives, as has been shown by nuclear magnetic resonance. The presence of bulky ligands on the titanium impedes rotation of the rings, probably owing to the "catching" of hydrogen atoms in rings located at an angle to one another [105].

Investigation of a large number of monocyclopentadienyl derivatives of titanium by infrared spectroscopy over the range 200–500 cm^{-1} has enabled an assignment to be made of the titanium–cyclopentadienyl ring and titanium–halogen stretching vibrations [106].

Nesmeyanov, Brainina, and their coworkers [107-109] developed several new methods for synthesising cyclopentadienyl compounds of zirconium and hafnium. They prepared and made a detailed investigation of novel types of compounds, such as cyclopentadienyl-oxans containing two metal atoms, mixed compounds containing zirconium (or hafnium), cyclopentadienyl rings, and chelate groups.

Nesmeyanov and Kritskaya studied π-allyl complexes of iron of the type tricarbonyl-π-allyliron halides and di-π-allyliron and carbonyl. In particular, they showed that the π-allyl groups underwent rotation about an axis passing through the centre of the plane of the allyl ligand and the iron atom. The magnitude of the rotational barrier depends on the nature of other groups present in the molecule [110-113].

The same workers have shown that complexes of π-benzyl type are formed comparatively easily with iron by fused aromatic systems starting with naphthalene. Several compounds have been prepared in which naphthylmethyl groups are simultaneously attached to iron by both π- and σ-bonds. π-Benzyls represent a novel type of ligands—the benzologues of π-allyl. [114]

III. ORGANOMETALLIC COMPOUNDS OF NON-TRANSITION METALS AND PROBLEMS OF CONJUGATION, DUAL REACTIVITY, AND TAUTOMERISM

During recent years Nesmeyanov's researches have been concentrated mainly on expanding the chemistry of organometallic compounds of the transition metals. Investigations on compounds of non-transition metals, which are still going on, represent mainly an extension of previously established lines of research, described in detail in a previous review [1]. Therefore they will be only briefly discussed below. During recent years these lines of research have already been independently continued by Nesmeyanov's students. They include the work by O. A. Reutov and his coworkers on the stereochemistry of the electrophilic substitution of a metal at saturated and ethylenic carbon atoms, a series of papers by I. F. Lutsenko et al. on organometallic derivatives of oxo-compounds, and several others.

In studying the properties, structural peculiarities, and effect of atoms and groups on the reactivity of organometallic compounds Nesmeyanov made a big contribution to the solution of important theoretical questions of general significance for chemical science. For example, the investigation by Nesmeyanov, Freidlina, and Borisov of β- and α-alkylated organometallic compounds ("quasi-complex" compounds) led not only to several general methods for the preparation of various compounds of this class and the solution of the hitherto controversial question of their structure but also to new ideas on the dual reactivity of substances, on the "transfer of the reactive centre" along a chain of $\sigma\pi$-, $\sigma\delta$-, $p\pi$-, and $p\sigma$-conjugation in a molecule, and to distinguishing these phenomena from those of tautomerism as equilibrium isomerisation. Many of these ideas have entered widely into the general practice of chemical research.

Nesmeyanov and Lutsenko expanded the investigation of this field by developing a method for the preparation of α-mercurated aldehydes and ketones as well as carboxylic esters, and studying their properties. Compounds having this structure were also found to exhibit dual reactivity.

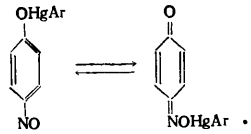
These investigations by Nesmeyanov and Borisov also laid the foundations of the stereochemistry of unsaturated organometallic and organoelementary compounds. They developed methods for the synthesis, separation, and identification of various β-substituted *cis*- and *trans*-unsaturated organometallic compounds, and established the main stereochemical laws in exchange reactions and the reduction of such compounds. These workers formulated the general rule that the geometrical configuration is maintained during electrophilic and radical substitutions at an ethylenic carbon atom [2]. The value of this rule is fully comparable with the well known rules of inversion and non-inversion of stereochemical configuration in the chemistry of optical isomers.

A series of papers by Nesmeyanov and Sazonova on the dual reactivity of metal (magnesium, lithium, sodium, etc.) derivatives of diphenylpropiomesitylene are closely related in concept to the investigation of quasi-complex compounds and α-mercurated oxo-compounds. These enolates were obtained in two stereoisomeric forms—*cis* and *trans*—which under certain conditions were incapable of mutual conversion, i.e. of tautomeric transitions [2]. The investigation under these conditions of the dual reactivity of these enolates served as the experimental basis for extending concepts of dual reactivity and migration of the reactive centre, developed in the study mainly of covalent mercury compounds, to the reactions of ordinary metallic derivatives of keto-enolic and other tautomeric systems and for generalising them throughout the field of tautomerism. Over this period Nesmeyanov has published a series of summary papers [115-117], devoted to problems of tautomerism and dual reactivity.

During recent years the further development of work on vinyl compounds of metals has led Nesmeyanov and Borisov to the synthesis of those of antimony, arsenic, tin, and germanium, and the preparation of ethylene derivatives containing two organometallic groups attached to the ethylenic bond, in which the metal atoms are either like or unlike [118-121]. The structure of β-chlorovinyl compounds of mercury has been confirmed by nuclear magnetic resonance, and the rate of acidolysis of the *cis*-isomer shown to be lower than that of the *trans*-isomer, in confirmation of Nesmeyanov's earlier concept of σπ-conjugation in these compounds and of a link between the geometric configuration of their molecules and their reactivity [122-124].

Nesmeyanov and his coworkers have developed a method for the synthesis of trichloromethyl- and polyhalogenomethyl-mercury salts and trichloromethylarylmercury, which are of interest as a source of halogenated carbenes which cannot be obtained in alkaline medium [125].

Nesmeyanov and Kravtsov have used spectroscopic methods in a broad investigation of the structure of organometallic derivatives of tautomeric and potentially tautomeric systems in which the bonds between metal and cation-acceptor centre are of low polarity. They have established that in most cases the organometallic derivatives have the structure of one of the two possible tautomeric forms, the nature of which depends on the character of the metal atom and the atom of the tautomeric substance [126-129]. Nevertheless, in the cases of the organomercury, organolead, and organotin derivatives of nitrosophenols this work resulted in the discovery of the phenomenon of metallotropy, i.e. the reversible migration of the organometallic grouping in the tautomeric system, and the position of tautomeric equilibrium was shown to depend on the nature of the solvent, of the organometallic grouping, and of substituents in the system, e.g. nitrosophenol [130]. Similar results were obtained for the *N*-organomercury derivatives of arylsulphonylaminopyridines [131]. It was then established for *N*-organomercury derivatives of halogenoimidazoles that intermolecular coordination in the crystalline state can lead to intermolecular mesomerism, in which the metal is simultaneously bound to both possible cation-acceptor centres in the tautomeric system [132]:



An analogous structure, intermediate between two possible states, is possible in intramolecular mesomerism, which is characteristic of the mercury and organomercury derivatives of cyclopentadiene [133]. Thus it has been shown that, depending on the character of the tautomeric system, the nature of the metal, and the physical state, every possible type of structure—(1) one of the extreme forms, (2) tautomeric equilibrium of the two forms, and (3) inter- and intra-molecular mesomerism—can be found in the metal derivatives of tautomeric systems. Thus to the only known form of cationotropy—prototropy—is added a new type—metallotropy.

Nesmeyanov's investigations on the structure of organometallic derivatives of tautomeric systems made it necessary to clear up several related questions of theoretical organometallic chemistry. In the course of this work it was established that the electronic effect of mercury-containing substituents is inductive in character, being markedly dependent on the nature of the solvent, and it was also demonstrated that organomercury, organolead, and organotin groups are capable of intramolecular coordination with halogen atoms [134-136].

IV. INVESTIGATIONS ON ORGANIC COMPOUNDS

Studies of dual reactivity and tautomerism belong equally to organometallic and to organic chemistry. Passing now to a brief account of certain new results of Nesmeyanov's researches in the field of organic chemistry, we may mention a series of papers (with R. Kh. Freidlina, E. I. Vasil'eva, F. K. Velichko, L. I. Zakharkin, Sh. A. Karapet'yan, V. N. Kost, R. G. Petrova, E. Ts. Chukovskaya, and others) on radical telomerisation and rearrangements of radicals, which have been partly described above [1]. At the present time investigations in this field are being conducted over a broad front by Nesmeyanov's students.

1. Investigations on β-Substituted Vinyl Ketones

A characteristic feature of Nesmeyanov's research activity is the close interlinking of three branches of chemistry—theoretical, organic, and organoelementary—which can be especially clearly traced in his work on β-substituted vinyl ketones [137,138].

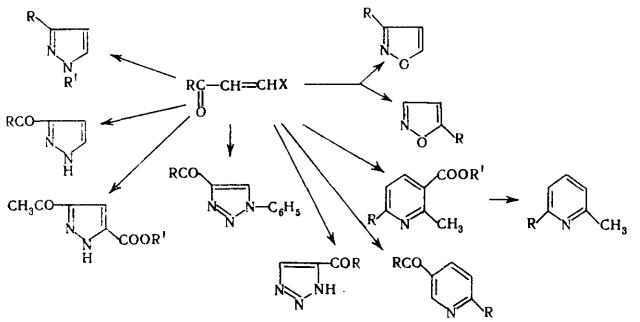
The high activity of the carbonyl group together with the mobility of the β-substituent in compounds of the type RCOCH : CHX was successfully exploited by Nesmeyanov Kochetkov, and Rybinskaya to develop methods for the synthesis of various five-membered nitrogen-containing heterocycles. Nesmeyanov, Kochetkov, and their coworkers used the same compounds to develop methods for the synthesis of pyridine derivatives (see Scheme 7).

Especially interesting examples of these heterocycles were cations isoelectronic with naphthalene and phenanthrene and containing an onium heteroatom $\dot{O}=$ or $>\dot{N}=$. Thus the reaction of β-chlorovinyl ketones with phenols and 2-naphthol was used to develop a method for the synthesis of benzopyrylium, flavylium, and naphthopyrylium salts. Subsequently the synthesis has been accomplished of heterocyclic cations containing an ammonium nitrogen atom in a bridge, so called dehydroquinolizinium salts and their 1-aza- and 1,9-diaza-analogues [138] (see Scheme 8).

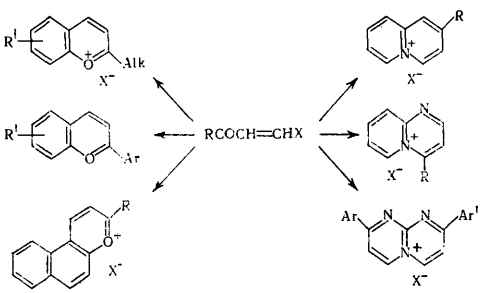
After the rule that geometrical configuration is maintained during electrophilic and homolytic substitution at an ethylenic carbon atom had been formulated, Nesmeyanov, Kochetkov, and Rybinskaya undertook a study of the

stereochemistry of nucleophilic substitution, choosing β-substituted vinyl ketones as model compounds. This investigation required a great amount of preliminary work, which involved developing a broad synthetic method, termed β-ketovinylation [138]. The reaction of β-ketovinylation, which is now taken to imply the introduction of a ready made RCOCH : CH group into a molecule, has permitted the preparation of the most diverse *cis*- and *trans*-β-substituted vinyl ketones. The ketovinyl fragment in these compounds was combined with atoms of various elements, such as carbon, nitrogen, oxygen, sulphur, hydrogen, iron, cobalt, and tungsten. Development of the method of ketovinylation resulted in the synthesis of organic compounds of various classes. In the course of this investigation the choice of ketovinylating agent was shown to be very important, and basic principles for such choice were formulated. For example, β-chlorovinyl ketones can be used for the ketovinylation of weakly basic and strongly polarised anions such as SCN^-, $SC_6H_5^-$, $SO_2C_6H_5^-$, N_3^-, etc., whereas in the case of strongly basic and relatively unpolarised nucleophiles (Alk, Ar^-, H^-, NH_2NH_2) the reaction leads to an addition product involving the carbonyl group [138]. This example thus provides evidence that, in the choice of ketovinylating agent, the selectivity of nucleophilic reagents towards a definite reaction centre has to be taken into account. For the ketovinylation of strongly basic and weakly polarised nucleophiles, therefore, the use of β-dimethylaminovinyl ketones was recommended. Furthermore, very active quaternary β-acylvinyltrimethylammonium salts were proposed [138] for very weakly nucleophilic anions ($OCOCH_3$, NO_2, etc.).

Scheme 7

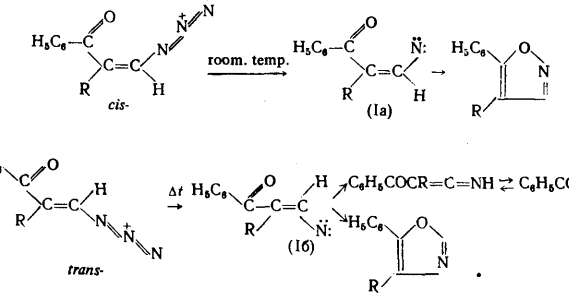


Scheme 8



As a result of this large amount of synthetic work it was found that the most convenient model reaction for studying the stereochemistry of nucleophilic substitution at an ethylenic reaction centre is the reaction of compounds C_6H_5COCR : CHX with the azide ion in various media.

Nesmeyanov and Rybinskaya showed by means of this reaction that the stereochemical course of nucleophilic substitution at an ethylenic carbon atom depends on the nature of the group X which is eliminated. For substrates having X groups (such as the chloride anion) which are "readily removable" as anions it was found that the geometrical configuration was preserved. In the case of "slowly removable" groups X (such as $C_6H_5SO_2$) the reaction resulted mainly in formation of the thermodynamically more stable isomer; and with "very difficultly removable" groups (X = CN, SO_3^-), reaction with the azide ion yields, instead of β-azidovinyl ketones, the isomeric 4-acyl-1,2,3-triazoles. The stereochemical results obtained in this way enabled a mechanism of direct substitution with intermediate formation of carbanions to be suggested for nucleophilic substitution at an activated double bond, and this is supported also by kinetic investigations [138]. A very interesting rearrangement was studied on β-azidovinyl ketones as example, which showed that stabilisation of the intermediate nitren species (Ia and Ib) depends mainly on its configuration:



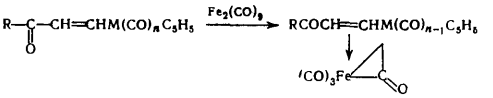
Very interesting compounds, β-aminovinyl ketones, were prepared by β-ketovinylation, and these exhibited a new type of tautomerism, ketiminol ⇌ enamineketone [138].

Another line of research deriving from the study of ketovinylation reactions was concerned with determining the orientation of nucleophilic attack in XCH : CHY systems, where X and Y are strong electron-acceptor groups. The kinetic investigation by Nesmeyanov, Rybinskaya, and Rybin led to a hypothesis which enabled the orientation of nucleophilic attack for systems of this type to be predicted by comparing data on the kinetic or thermodynamic acidities of the corresponding methyl derivatives CH_3X and CH_3Y. These workers started from the view that the orientation of nucleophilic attack should depend on the relative stability of the intermediate carbanions XCH–CHYZ and XZHCH–CHY (where Z is the nucleophilic reagent) [137].

The chemistry of β-substituted vinyl ketones has recently been considerably added to by the investigations of Nesmeyanov and his coworkers on σ- and π-complexes of transition metals, in which β-substituted vinyl ketones were used as ligands. The employment of complex anions $[Fe(CO)_2C_5H_5\text{-}\pi]^-$, $[W(CO)_3C_5H_5\text{-}\pi]^-$ (pyridinatocobaloxime)$^-$ in ketovinylation led to synthesis of the complexes σ-RCOCH : CH.ML_n (where M is a transition metal and L a unidentate ligand). [138]

However, β-substituted vinyl ketones have been most widely used for the preparation of σ-complexes with iron carbonyls [139–142], in which it was possible to trace qualitatively the variation in the complexing power of RCOCH : CHX with the nature of the substituent X. This investigation showed that π-complexes are not formed from ligands containing strongly electron-donor groups (e.g. X = $NAlk_2$) or from RCOCH : CHX in which X = CN, NO_2. In the

latter two cases polymers were isolated having a non-stoichiometric iron content. Stable complexes were obtained only from ligands having X = Cl, SO_2R, COOR, COC_6H_5. Comparison of these results with the calculated energies of antibonding orbitals for the corresponding ligands showed that this energy is too high for a stable π-complex to be formed in the case of RCOCH : CHNAlk$_2$ and too low for the ligands RCOCH : CHX (X = CN, NO_2). The formation of polymers having a non-stoichiometric iron content was explained by the possibility of complete transfer of an electron from the metal to the ligand. The radical-anion obtained $(RCOCH : CHX)^{\cdot -}$ could in turn give rise to a polymeric chain. It is interesting that on π-coordination with metals the ligands maintained their original configuration. Investigation of σ-ketovinyl complexes in reactions with $Fe_2(CO)_9$ enabled Nesmeyanov and his coworkers to obtain a series of novel mixed dinuclear $\sigma\pi$-complexes of type (II), characterised by a metal–metal bond and a bridging carbonyl group:



(II)

where M = Fe, n = 2 and M = W, n = 3.

2. Onium Compounds

The first investigation of this series was made in 1929, when Nesmeyanov examined the decomposition of the double salts formed by diazonium compounds with mercury(II) iodide, and established the formation of iodonium salts [143]:

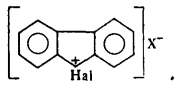
$$C_6H_5N_2HgI_3 \text{ and } (C_6H_5N_2)_2HgI_4 \rightarrow [(C_6H_5)_2HgI_4] + N_2 \ .$$

Some of the most recent (1967) work on these lines is described in a paper on the reactions of arenediazonium fluoroborates with substituted iodobenzenes, which showed the effect of the nature of nuclear substituents both in the diazonium salt and in the iodobenzene on the yield of diaryliodonium salts [144].

A set of methods was developed constituting the onium synthesis [2], based on transfer of the aryl radical or aryl cation of the onium compounds to a metal atom, salts, unsaturated compounds, and substances containing atoms having a lone pair of electrons—O, S, Se, N, P, As, Sb, Cl, Br, I.

The most general results of these investigations include firstly the establishment of two types of decomposition of diazonium, iodonium, and certain other onium salts with transfer of aryl cations or aryl radicals [145]. Conditions which determine the type of decomposition have been worked out (effect of structure of aromatic nucleus of onium compound, nature of salt anion, nature of substrate (aryl acceptor), nature of solvent, presence of catalyst, etc.). The rules established by Nesmeyanov together with Makarova, Tolstaya, et al. for the directed synthesis of various compounds from diazonium or other onium salts are now widely used in synthetic practice (e.g. the synthesis of arylisothiuronium salts by the reaction of arenediazonium fluoroborates with thiourea [146,147]).

Another most important result of this work was the contribution of the onium method to the synthesis of previously unknown types of compounds of multivalent chlorine, bromine, oxygen, nitrogen, and sulphur. Thus, in contrast to compounds of multivalent iodine, which have been known for a long time, the simplest compounds of multivalent chlorine and bromine—diarylchloronium and diarylbromonium salts—were unknown before the work of Nesmeyanov, Tolskaya, and their coworkers [148,149]. Only heterocyclic compounds of this type were known previously [150]:



It appeared that a heterocyclic position of the halogenonium grouping was a necessary condition for the existence of sufficiently stable halogenonium compounds. However, Nesmeyanov, Tolstaya, and their coworkers obtained numerous symmetrical and unsymmetrical diaryliodonium and diarylbromonium salts, as well as heterocyclic compounds of this type. The synthesis of diarylchloronium and diarylbromonium salts was accomplished by the reaction of arenediazonium fluoroborates with aryl halides:

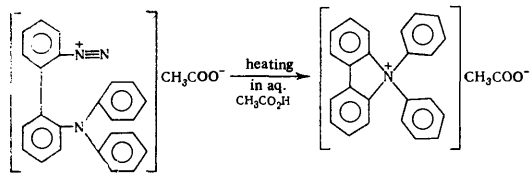
$$ArN_2BF_4 + Ar'Hal \rightarrow [ArAr'Hal]^+BF_4^- \xrightarrow{+X^-} [ArAr'Hal]^+X^- \ .$$

It proved possible to prepare the hitherto unknown triaryloxonium salts by the same method [151]:

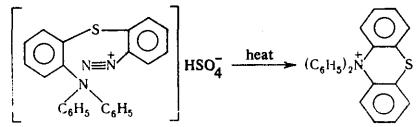
$$ArN_2BF_4 + Ar_2O \rightarrow [Ar_3O^+]\,BF_4^- \xrightarrow{X^-} [Ar_3O^+]\,X^- .$$

In contrast to Meerwein's trialkyloxonium salts [152,153], triphenyloxonium salts are extremely stable compounds, decomposing only when heated above 150°C.

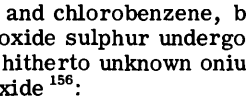
Completely aromatic onium compounds had been known for all elements other than nitrogen in the main subgroup of Group V of the Periodic System. Tetra-arylammonium salts could not be obtained by the arylation of triphenylamine with diphenyliodonium fluoroborate. Compounds of this type, namely *NN*-diphenylcarbazolium salts, could be prepared [154] by the reaction



The same workers have recently described the preparation and properties of another fully aromatic ammonium cation, *NN*-diphenylphenothiazinium [155]:



When benzenediazonium fluoroborate decomposes in a mixture of dimethyl sulphoxide and chlorobenzene, bromobenzene, or acetone, the sulphoxide sulphur undergoes arylation with the formation of hitherto unknown onium salts of dimethyl phenyl sulphoxide [156]:



Nesmeyanov and his coworkers have made a broad investigation of the reactions of the newly prepared onium compounds. They have shown, for example, that diphenylchloronium and diphenylbromonium salts are nitrated in the *meta*-position, thus conforming to the general rule of orientation in the nitration of aromatic onium compounds. On the other hand, the nitration of triphenyloxonium fluoroborate, which could be accomplished only under severe

conditions (with a mixture of anhydrous nitric and concentrated sulphuric acids at 100°C), yields tri-*p*-nitrophenyloxonium fluoroborate. The nitration of triphenyloxonium fluoroborate by means of nitryl tetrafluoroborate takes place even at room temperature and also leads to the same tri-*p*-nitrophenyloxonium fluoroborate.

The explanation given for the unusual behaviour of the triphenyloxonium cation was that the strong negative inductive effect of the oxonium oxygen, which inactivated the phenyl rings, was nevertheless associated, as in the halogenobenzenes, with conjugation of the lone pair of electrons on the oxygen atom with the π-electrons of the phenyl (+ *T*-effect).[157]

Tri-*p*-nitrophenyloxonium fluoroborate was reduced to the corresponding amino-derivative. The basic properties of the amino-groups in tri-*p*-aminophenyloxonium salts are appreciably weakened under the influence of the oxonium oxygen. These amino-groups are diazotised only under conditions for the diazotisation of weakly basic amines, e.g. by the action of nitrosylsulphuric acid. The tri-*p*-aminophenyloxonium cation is formally analogous in structure to the parafuchsine cation, but, unlike the latter, is colourless[158]. Explanations are given for this difference. For the infrared spectra of diphenylhalogenonium and triphenyloxonium compounds see Ref. 159.

Quite recently Nesmeyanov has shown, together with Makarova, Chapovskii, and Ustynyuk, that a rylation by diazonium and other onium compounds can be used for the synthesis of σ-aryl derivatives of transition metals. The action of benzenediazonium, diaryliodonium, and triphenylsulphonium salts on the anions of cyclopentadienylcarbonyl-iron[160,161], -tungsten[162], and -molybdenum[163] has yielded their σ-aryl derivatives. Thus the σ-phenyl derivative has been obtained by the interaction of triphenylsulphonium fluoroborate with the sodium salt of π-cyclopentadienyldicarbonyliron:

$$\pi\text{-}C_5H_5Fe(CO)_2Na + [(C_6H_5)_3S^+]\,BF_4^- \rightarrow \pi\text{-}C_5H_5Fe(CO)_2C_6H_5 \ .$$

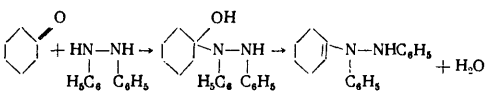
Let us make a brief mention of Nesmeyanov's work on hydride migration. In 1960 Nesmeyanov and Golovnya showed for the first time that the nitrogen atom in the azo- and diazo-groups of organic compounds can act as an acceptor for hydridic hydrogen, being more vigorous than the carbonium cation[164]. Salts of azobenzene with electrophilic reagents such as boron trifluoride, sulphuric acid, hydrobromic acid, hydrochloric acid, orthophosphoric acid, zinc chloride, etc. were able to remove hydride hydrogen from most organic solvents.

The surprising ability of azobenzene to abstract hydrogen from compounds which are so stable to oxidation as benzene, nitrobenzene, cyclohexane, and n-hexane, the ease of occurrence of the reaction with cycloheptatriene, and also the absence of reaction with chloroform and nitromethane led these workers to suggest the following reaction mechanism

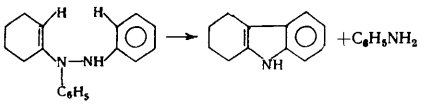
$$[C_6H_5{-}NH{=}N{-}C_6H_5]^+HSO_4^- + H{:}\,C\!\!<\!\!\rightarrow C_6H_5NH{-}NH{-}C_6H_5 + \overset{+}{C}\!\!<\!\!\rightarrow + HSO_4^-$$

$$C_6H_5NH{-}NH{-}C_6H_5 + H_2SO_4 - (NH_3^+C_6H_4)_2SO_4^{2-} \ .$$

In the course of their investigation[164] Nesmeyanov and Golovnya discovered a new variant of the classical Fischer–Arbuzov synthesis of indoles. They showed that in the presence of boron trifluoride azobenzene reacts with cyclohexanone to form tetrahydrocarbazole. The reaction takes place also with homologues of cyclohexanone. The first stage is reduction of the azobenzene by hydride hydrogen abstracted from the cyclohexanone, the resulting hydrazobenzene reacts with the ketone to give the corresponding one–hydrazine:



and this cyclises to tetrahydrocarbazole with the elimination of aniline (not ammonia, as in the usual indole ring-closure):



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Institute of Organoelementary Compounds, USSR Academy of Sciences, Moscow

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Development of Chemical Investigations on Artificial and Synthetic Foods.

V.M.Belikov, S.V.Rogozhin, G.L.Slonimskii, R.V.Golovnya, and B.V.Tolstoguzov

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I. INTRODUCTION

The idea that it was opportune for the start of practical studies on the production of food by industrial methods, avoiding agriculture, was suggested by A. N. Nesmeyanov at the beginning of 1961. This idea was based on the one hand on the work of the great chemists of the past—D. I. Mendeleev and M. Berthelot—and on the other, on an understanding of the contemporary state of the science of the physiology of nutrition and the achievements of the chemical industry[1]. Actually, at this time it appeared that man could satisfy all his physiological requirements by living exclusively on rations consisting of substances made synthetically. This gave a confidence in the knowledge of the main ingredients of food.

The great output of organic synthesis, which reaches millions of tonnes per annum in the production of polymeric products, made the question of the creation of a food products industry a real subject. Thus were all the proteins needed for feeding a country with a population of 250 million to be produced industrially it would be necessary to make about 6 million tonnes per annum.

Moreover, at this time the problem of the shortage of foodstuffs, especially proteins, became very acute. According to United Nations Organization data, about two-thirds of the population of the world are now in a state of chronic malnutrition, and often complete starvation[2].

No less alarm is aroused by the progressive destruction of the Earth's exposphere and the associated depletion of natural resources[3].

Hence in contrast to the XIXth century there were the need and real reasons for a practical solution of the problem of the production of synthetic food. There still remained one difficulty without overcoming which it would be impossible to think of the propaganda of new ways of obtaining food. This difficulty consists in the high cost of synthetic foodstuffs used for making synthetic rations. These substances—amino-acids, fatty acids, some vitamins—sold as reagents would be excessively dear. But economics should in the final analysis decide the choice between various methods for obtaining food. Furthermore it would be necessary to give the synthetic mixtures taste in the widest meaning of this word, including odour, taste itself, form, texture, etc.

To solve all these problems laboratory investigations were made under the guidance of A. N. Nesmeyanov in the Order of Lenin Institute of Organoelemental Compounds of the Academy of Sciences of the USSR into the production of edible amino-acids, proteins, and other foodstuffs, the study and reproduction of pleasant natural odours of prepared food, and the physical and chemical processes of structure formation. The need arose for the development of a series of theoretical and practical problems of biochemistry, organic, physical, and analytical chemistry and the foundations of a new branch of science—that of synthetic food—were really laid.

On comparing the various paths for the industrial production of foodstuffs that now most promising is microbiological synthesis. Nesmeyanov first understood the great potential possibilities of this method and under his initiative complex studies on the growing of yeasts on petroleum hydrocarbons were undertaken in the Soviet Union in 1963. As a result, by 1967 several experimental industrial plants for yeast bio-mass had been commissioned.

This bio-mass contains ~40% protein rich in amino-acids, as well as fats and vitamins. It is now being used as an animal food product but it is much more profitable to use these yeasts directly in human nutrition[3]. Naturally for this the beneficial constituents should be separated, freed from ingredients having doubtful nutritive value, and converted into an edible form with the necessary odour and taste.

The present review deals with the studies, mainly under the leadership of A. N. Nesmeyanov, directed to the solution of this problem.

2. PROTEINS AND NUTRITION

Most of the amino-acids needed for active life are obtained by man in the form of various proteins present in the products of plant and animal origin. The great protein deficiency makes the problem of increasing the effectiveness of the use of food proteins very acute and also that of acquiring new unusual sources of proteins which can be used for solving the problem of nutrition directly or through animal husbandry.

The first path—the use of proteins of unusual origin directly in human food—is the more promising, since shortening the nutritive chain increases the effectiveness of use of the proteins by a factor greater than five, that is, to bring about the same results much less protein must be made than in the production of protein food products by traditional methods via animal husbandry[1].

In addition, the separation from various sources of proteins with their simultaneous purification from extraneous substances, sometimes also harmful impurities, enables not only the biological value of the proteins when

used in nutrition to be increased but also food products to be obtained with the required amino-acid composition and with many other nutritive components of the necessary composition, taken in optimal amounts, that is, to convert the foodstuffs into a sufficiently powerful means of regulating the biochemical processes of the human organism.

Table 1. Principal oil-bearing crops.

Name	Mean protein content, %	Lipid content, %	World production, tonnes	Chief producing countries	Factors preventing use for food
Soya bean	42	20	35 000	U.S.A., China	inhibitors of trypsin, chemotrypsin, haemoglutinin, saponins
Groundnut	27	48	14 800	India, Senegal, Nigeria	aflotoxins, saponins
Cotton seed	30	30	20 600	U.S.A., India, U.S.S.R., Mexico, U.A.R., Brazil, Pakistan	gossypol, aflotoxins
Eastern sesame	25	50	1500	China, India, Sudan Mexico	oxalates, fibres
Sunflower seed	30	40	6840	U.S.S.R., Argentina, Uruguay, South Africa, Turkey	fibres

Apart from the usual animal and plant sources of proteins already recommended in nutrition, there is a large number of sources of sufficiently rich proteins, especially plant proteins, which are not widely used in nutrition owing to accompanying impurities. Table 1 gives information about the world production of oil-bearing crops containing large amounts of proteins, sufficiently rich in nutritive respects [4]. However, cotton seeds, which are rich in protein, contain the toxic substance gossypol, soya beans contain a series of growth inhibitors and inhibitors of digestive enzymes, castor plant seeds contain ricin and several allergins, and certain fruits contain glucosides which liberate cyanides and various inhibitors of biological processes [5]. Naturally, such protein products can be widely used in nutrition only after isolating the proteins and freeing them from the harmful impurities.

Table 2.

Components	*Torula*	*Candida tropicalis*	Components	*Torula*	*Candida tropicalis*
Dry substances, %	93.0	92.7	Vitamins, mg per kg		
Protein (total), %	34.0	43.6	thiamin (B_1)	80	3.16
Carbohydrates, %	34.0	21.0	riboflavin (B_2)	120	75
Fats, %	7.8	18.5	nicotinic acid (P-P)	800	180—200
Inorganic substances (ash), %	7.5	4.43	panthothenic acid (B_3)	47	150—192
			pyridoxin (B_6)	26	23

There are still richer sources of valuable proteins in the micro-world among the various algae, yeasts, and non-pathogenic micro-organisms [6-9]. Thus the widely distributed yeasts of the *Candida tropicalis* and *Torula* cultures, the basis for the growth of which are wastes from the alcohol industry and hydrocarbons, are rich sources of valuable proteins [10] (Table 2).

The exceptionally high rate of synthesis of proteins by micro-organisms and also the possibility of the organization of their production on a large scale by industrial methods offers great possibilities for rapidly increasing protein resources by microbiological means. The results given in Table 3 on the rate of accumulation of bio-masses by various organisms show that the rate of synthesis of proteins by micro-organisms is more than 1000 times the rate of synthesis of proteins by higher organisms.

Table 3. Time for a twofold increase in the biomass of growing organisms in the phase of maximal growth [11].

Organism	Time, h
Bacteria and yeasts	0.3—2
Fungi and chlorella	2—6
Grass and plants	144—288
Chicks	288—576
Piglets	576—864
Beef cattle	720—1500

It is noteworthy that unlike most plant proteins, which are often deficient in lysine, tryptophan, and methionine, the proteins which are synthesised by micro-organisms are considerably closer in composition to animal proteins and can be readily assimilated in an isolated state.

Despite repeated attempts to use various yeasts in human nutrition without separating the proteins from them, especially under unusual conditions (war, drought, etc.), microbiological products have not yet found wide application in nutrition without additional chemical treatment owing to several of their properties (flavour, odour, appearance).

One of the possible ways of using valuable foodstuffs which are present in microbiological raw material, and above all in various yeasts consists in the isolation from the hydrolysis products of the microbiological raw material of all the amino-acids suitable for use in human nutrition.

No less promising is the isolation from the micro-biological raw material of all the proteins it contains, their purification, and use directly in foods. In this instance all the factors (colour, odours, and extraneous flavour) which hinder the wide use of new sources of proteins in nutrition can be removed, which simultaneously increases the biological value of such proteins. For example, Mitsuda and coworkers [12] showed that the proteins isolated from *Micrococcus glutamicus* does not differ in amino-acid content from the protein of hen's eggs.

The amino-acid composition of the microbiological proteins isolated (Table 4) shows that they are much more balanced than plant proteins.

In determining the food value of the total proteins isolated by extraction with urea from a *Torula* strain it was found that the product isolated is assimilated and converted much better than entire yeast cells [13]. When chlorella with unbroken cells was used as a source of proteins similar results were obtained. Here it was found that > 40% of the nitrogen was not absorbed in the gastrointestinal tract [14].

The zooplankton of the Pacific Ocean can be a vast source of proteins [15], and their role for increasing the protein resources becomes real after the development of

accessible and economically favourable methods of separation and purification of proteins present in marine microorganisms.

The need for the thorough purification of microbiological proteins destined for food purposes is also confirmed by the investigation of the biological value and harmlessness of the protein–vitamin concentrate obtainable from yeasts cultivated on hydrocarbons and at present usable only as animal food [16,17].

Table 4. Amino-acid composition of proteins in % of the sum of the ten most important amino-acids.

Amino-acid	Products								
	meat (pork)	dried milk (fat-free)	whole egg	protein of *Micrococcus glutamicus*	protein of the yeast *Torula*	white bread	oatmeal	ground-nuts	corn-flakes
Arginine	11.8	6.0	10.3	14.4	—	9.5	12.3	30.1	4.4
Valine	10.7	13.3	12.1	14.1	8.8	15.9	13.1	9.7	12.2
Isoleucine	9.9	10.5	9.9	11.1	13.4	12.0	9.7	8.3	9.3
Leucine	18.4	19.5	15.9	17.3	18.2	20.4	19.0	14.7	39.2
Lysine	16.8	16.3	13.1	12.3	21.0	7.3	8.1	8.7	1.8
Methionine	5.5	4.9	6.1	3.8	1.2	3.8	4.6	2.1	4.9
Thionine	8.9	8.8	8.6	9.2	12.8	8.9	8.7	5.7	8.5
Tryptophan	2.8	3.1	2.9	2.8	2.4	3.7	2.8	2.6	1.5
Tyrosine	6.9	8.3	7.2	5.4	10.0	5.7	7.7	6.5	4.6
Phenylalanine	8.3	9.4	9.4	9.3	11.9	14.1	14.2	11.4	13.5

The extraction and purification of proteins from microbiological raw materials are also necessary for the subsequent creation from them of edible forms suitable for human beings. Most of the products for feeding human beings have a complex structure consisting of three main elements—fibres, films, and gels, which can be obtained and even now are being made for technical purposes in industry [18] from proteins which are polymers of α-amino-acids.

Proteins, like mixtures of amino-acids, are white powders, almost devoid of odour and taste, of little use in this form for food. However, the complex of physicochemical properties of proteins allows any structural elements of the usual nutritive forms to be obtained from them and new nutritive forms based on them to be created, as shown below.

As is well known, after fermentation and separation from the culture medium the bio-mass contains many substances of nutritive value: up to 40% (on the dry weight) of proteins, a certain amount of free amino-acids, fats, polysaccharides, vitamins, nucleic acids, and various other compounds. From the chemist's viewpoint a single-cell organism is a complex system consisting of polymers of three types and a large number of low-molecular-weight compounds entering both into the composition of cell walls, membranes, and other structural elements of cells and also found in protoplasm.

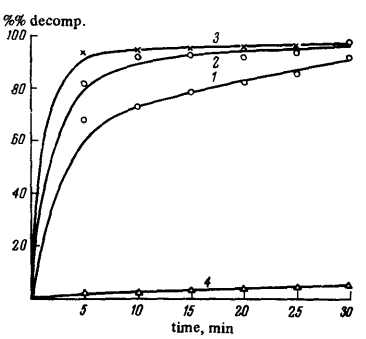
Owing to the semipermeable nature of the cell membranes and other structural formations of the cells, part of the low-molecular-weight compounds—inorganic salts, vitamins, free amino-acids, and part of the lipids—can be separated from the cell material without destroying the cell and its structural elements.

In accordance with their chemical nature, proteins usually dissolve comparatively readily in water or aqueous salt solutions at various pH values, depending on the nature of the protein, and the resulting solutions can be isolated pure. However, owing to the insolubility of the outer sheath of unicellular organisms and the polymeric nature of the proteins their isolation in a pure form without destruction of the cell membranes is almost impossible.

In the literature there are several descriptions of methods of extracting native proteins from microbiological material in which the foremost aim pursued was to retain the enzymic activity of the proteins, their supermolecular structure, and also to obtain narrow protein fractions and, if possible, individual proteins [19-21]. These methods are usually distinguished by low reproducibility, complexity of the technical procedure, and low suitability for obtaining proteins in large amounts.

By using experience on the production of finely disperse aluminium for the synthesis of Ziegler catalysts for the polymerisation of ethylene, success was achieved in creating a method of breaking down the cell material in sufficiently large amounts (1 kg of dry material per operation). As a result of a large number of experiments it was found that at 10–15°C there is almost complete destruction of the cell walls in 15–20 min.

It was found that the effectiveness of the destruction of the cell walls depends on the nature of the medium in which the destruction is carried out; thus the Figure shows the change in the degree of destruction of the cell walls, calculated from the results of electron microscopy in different media depending on the time and temperature.



1) Hexane +7°C; *2*) hexanes −70°C; *3*) methylene chloride −70°C; *4*) water, +2°C.

As the Figure shows, water is quite unusable for these purposes. The most suitable medium for the destruction of the cell walls was methylene dichloride, widely employed in the production of acetate silk. The destruction is just as effective in other low-boiling dehydrated organic solvents: diethyl ether, acetone, alcohol, etc. The great merit of the method is its universality which allows proteins to be obtained from various microbiological and plant sources.

The destruction of cell membranes in methylene dichloride, in which alkanes and lipids dissolve readily, is accompanied by effective extraction of fats and hydrocarbons from the microbiological material and also of fat-soluble vitamins, which can then be isolated from the extractant and used. Complete extraction of the lipids greatly facilitates the further separation of the proteins and ensures a higher degree of purity of the final product.

After thorough removal of the organic solvent the broken-down cell material can be used for the isolation of nucleic acids and proteins.

Nucleic acids, which as a result of enzymolysis are converted into nucleotides [22] from which sodium inosinate and guanylate—the best taste-developing additives—are removed in the form of nucleoprotides by extraction with 10% NaCl. The proteins are transferred into the solution after extraction of the nucleic acids by treatment of the disrupted cell material with dilute alkali solutions (0.2M NaOH) and are purified by reprecipitation with hydrochloric or acetic acid or by electrolysis. The residues of the cell walls and other structural fragments of the cells in the isolation of the nucleic acids and proteins are separated from the solutions by centrifuging or filtration.

Table 5. Amino-acid composition of microbiological proteins and proteins of animal origin.

Amino-acid	Mouse actin	Casein	Protein of the yeast *Candida tropicalis*	Protein from *Saccharomyces cerevisiae*	Protein from *Micobacterium rubrum*	Protein from chlorella
Alanine	5.7	3.4	5.7	6.2	8.2	7.0
Arginine	5.9	3.9	3.9	4.2	8.1	4.1
Aspartic acid	9.8	7.6	10.6	10.0	7.4	7.8
Valine	4.4	5.7	5.4	5.5	7.0	3.4
Histidine	2.3	2.6	2.2	2.1	1.6	1.2
Glutamic acid	13.3	20.3	11.5	12.6	12.2	9.6
Glycine	4.7	2.1	4.2	4.4	4.0	4.7
Isoleucine	6.8	5.8	5.7	5.4	3.9	2.3
Leucine	7.4	7.1	8.8	6.9	7.3	5.3
Lysine	6.8	8.1	7.2	9.2	3.2	5.7
Methionine	4.0	2.3	2.2	1.2	1.6	1.8
Proline	4.6	6.9	3.6	4.0	2.2	3.6
Serine	5.3	5.7	3.8	5.2	2.5	3.5
Tyrosine	5.2	7.3	4.4	3.6	1.9	2.9
Threonine	6.3	4.4	4.1	5.4	4.1	4.1
Tryptophan	1.8	1.5	1.5	1.3	1.2	1.3
Phenylalanine	4.3	4.1	5.4	4.7	3.5	3.0

Note: The data for mouse action and casein are given in the Ajinomoto catalogue, Part 4, 1965. The amino-acid analysis of the microbiological proteins was obtained on an automatic analyser of Czechoslovak manufacture. The results for the last two products are rather low, owing to their containing carbohydrate impurities.

The yield of proteins in laboratory experiments is 65–75% (25–29% of the dry weight) at a purity of 80–95%. The protein products obtained do not contain mineral impurities (ash < 0.5%) or nucleic acids (traces of phosphorus) or organic impurities of a lipid or hydrocarbon nature. The only impurity in the product is 10–15% oligosaccharides entering into the composition of the cell walls, which can be removed by additional purification if necessary.

The amino-acid composition of the total proteins obtained (see Table 5), especially from yeast cultures, shows the exceptionally high value as a future source of rich nutritive proteins, since they are very similar in composition to the best proteins of animal origin (proteins of milk, meat, etc.).

The determination of the concentration in the initial material and in the liberated proteins of the three limiting amino-acids—tryptophan, methionine, and lysine—and also the determination in them of the available lysine convincingly confirms that in the separation and purification the biological value of the microbiological proteins is greatly increased (Table 6).

Table 6. Amino-acid contents of microbiological raw material and of the proteins isolated, obtained on its basis.

Name of initial material	Tryptophan, % calculated on proteins		Methionine, % calculated on proteins		Total lysine, %, calculated on proteins		Available lysine %, calculated on proteins		Ratio of available to total lysine	
	initial material	total proteins	initial material	total proteins	initial material	total proteins	initial material	total proteins	initial material	total proteins
Candida tropicalis	0.88	1.52	1.33	2.10	6.60	7.40	5.47	6.82	0.82	0.92
Saccharomyces cerevisiae	0.93	1.27	1.37	1.75	8.78	9.20	6.25	7.92	0.71	0.86
Micobacterium rubrum	0.83	1.20	1.42	1.82	4.51	5.18	3.16	3.59	0.70	0.69
Chlorella	1.51	1.53	1.98	2.10	7.53	5.30	4.52	4.55	0.60	0.85

It is quite natural that the possibility of using such isolated proteins directly for human nutrition will be determined after detailed biomedical investigations both of proteins themselves and of new food products based on their use. In their physicochemical properties the isolated proteins from yeast cultures are very similar to casein and completely suitable for obtaining granulated food products of the artificial-albumen caviar type, the method for making which was developed in the Institute of Organoelemental Compounds. The specimens of black granular roe obtained by using yeast proteins did not differ in either physico-mechanical or organoleptic properties from the roe obtained from milk casein.

3. AMINO-ACIDS

In recent years important results have been obtained in studying human nutrition with mixtures of amino-acids, although much still remains to be done. It seems definite that in maintaining the nitrogen balance of the human organism it is immaterial whether the person is fed with proteins or the mixtures of the constituent amino-acids.

Table 7. Amino-acid composition of a diet.

Amino-acid	Quantity, g day^{-1}	Amino-acid	Quantity, g day^{-1}
Isoleucine	1.78	Phenylalanine	2.42
Leucine	2.60	Tyrosine	0.66
Lysine	3.60	Threonine	1.21
Methionine	1.88	Tryptophan	0.62
Cysteine	0.31	Valine	1.78

Many investigations on the prolonged feeding of people with synthetic diets have been published recently [23–28]. As an example there is the amino-acid composition of the diet [23], used for feeding 22–25 year old men (Table 7). The remaining (replaceable) nitrogen was given in the form of a 1 : 1 (by weight) mixture of glycine and diammonium citrate. Evidently this mixture is the best source of exchangeable nitrogen [29–31].

The use of such diets no longer in medicine but for food purposes can be limited on the one hand, by the need for their texturing and culinary treatment, and on the other by the possible high cost of individual natural amino-acids. As regards the texturing, the studies which will

be described below have shown that this obstacle can be overcome. As regards cost, progress in the synthesis of amino-acids achieved in recent years gives a basis for hoping that there will be no significant difficulties here.

A very promising method for obtaining mixtures of edible amino-acids is by growing unicellular micro-organisms (usually yeasts on carbohydrate or hydrocarbon raw material), hydrolysis of the proteins thus obtained to amino-acids, and their isolation in pure form.

The growing of yeasts has now been developed very well and is carried out on an industrial scale. The bio-mass thus obtained contains ~40% proteins. The action of proteolytic enzymes on this bio-mass leads to the hydrolysis of the protein molecules [32].

The sum of chromatographically pure amino-acids can be isolated from the product thus obtained. To do this displacement ion-exchange chromatography is used [33]. The solution is passed successively through cation-exchange and anion-exchange resins and the amino-acids, as amphoteric compounds, are separated from all the other impurities which are not amphoteric. The product is a white powder completely soluble in water. The amino-acid composition corresponds to the amino-acid composition of the initial enzyme hydrolysate. The change of the amino-acid composition in the desired direction can be brought about by addition of a little of the pure amino-acids. In this form the product can be used as a basis for synthetic meat and other edible products, for constituents of synthetic diets, and also in various branches of medicine.

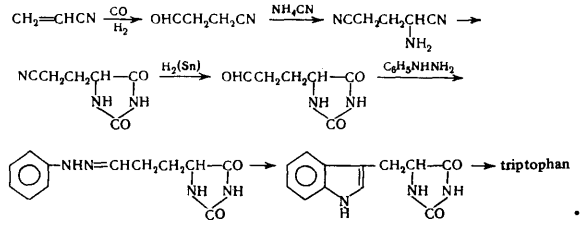
Many amino-acids are obtained on an industrial scale by microbiological means, by growing microbes which produce certain amino-acids on culture medium. The best results are obtained for *L*-glutamic acid and *L*-lysine [34]. The raw material usually employed is glucose or the cheaper molasses with the addition of ammonium salts as a source of nitrogen and of other salts required by the micro-organisms. However, there are results showing that alkanes can also serve as a source of carbon for the micro-organisms which produce amino-acids [35]. The most important precursor of glutamic acid—α-ketoglutaric acid—is isolated in the medium on growing certain strains of yeasts on a mixture of normal hydrocarbons of composition C_{14}–C_{26}. More than 800 g ketoglutaric acid are obtained from 1 kg alkanes [36].

In several instances a purely chemical synthesis is also economically suitable. An example is the production of *L*-lysine from caprolactam, effected by the Dutch firm of Stamicarbon on an industrial scale [37].

The industrial production of methionine in the USSR is based on the following scheme [38]:

$$CH_2{=}CHCHO + CH_3SH \rightarrow CH_3SCH_2CH_2CHO \xrightarrow{NH_3,KCN} CH_3SCH_2CH_2CHCN \rightarrow$$
$$\rightarrow CH_3SCH_2CH_2CHCOOH$$

In Japan there is a combined method for obtaining glutamic acid and tryptophan from acrylonitrile [39]. The part relating to tryptophan includes the following stage:



As regards threonine, the best method for making it can be considered to be the Akabori synthesis carried out on an industrial scale in Japan. The reaction consists in the interaction of copper glycinate with acetaldehyde in alkaline medium [40]. As our last investigations showed [41], a necessary condition for the occurrence of this reaction is the formation of a Schiff base, since if *L*-alanine is introduced into the reaction instead of glycine the rate of racemisation of its copper complex is very greatly increased in the presence of acetaldehyde and the methyl-threonine obtained is always racemised.

On the other hand, *NN*-dimethyl-*L*-alanine not only does not racemise in the presence of acetaldehyde but does not even give a hydroxyamino-acid.

In 1957 Nesmeyanov and Freidlin developed a new method of synthesis of ω- and α-halogeno-acids on the base of telomerisation. The amination of these compounds gives the most varied aliphatic, aromatic, and heterocyclic amino-acids [42].

Several new syntheses of the most important unsubstituted amino-acids have been described recently [43]. The most promising for industry of the synthesis is based on aliphatic nitro-compounds. The key substance in all these syntheses is nitromethane—a cheap and accessible substance. Nitromethane can be readily converted [44] into methyl nitroacetate, $O_2NCH_2CO_2CH_3$, a very reactive compound having a carboxyl group and a potential amino-group.

In the Institute of Organoelemental Compounds of the Academy of Sciences of the USSR and the Leningrad Pedagogic Institute syntheses of amino-acids from the nitroacetate have been developed, based on condensation with aldehydes, addition to an activated double bond, and alkylation of alkyl halides. Thus in the condensation of nitroacetic ester with acetaldehyde in the presence of catalytic amounts of sodium acetate α-nitro-β-hydroxybutyric ester is formed. Quantitative yield of the reaction product is observed when it is carried out in the absence of a solvent and at 10–12°C.

$$CH_3CHO + O_2N{-}CH_2COOCH_3 \xrightarrow{CH_3COONa} CH_3{-}\underset{\underset{OH}{|}}{CH}{-}\underset{\underset{NO_2}{|}}{CH}{-}COOCH_3 \xrightarrow[CH_3COOH]{H_2(Pd/C)}$$
$$\rightarrow CH_3{-}\underset{\underset{OH}{|}}{CH}{-}\underset{\underset{NH_2}{|}}{CH}{-}COOCH_3 \xrightarrow{H^+} DL\text{-threonine.}$$

The reduction of α-nitro- β-hydroxybutyric ester is effected over Pd catalyst in an autoclave [45].

Other α-amino-acids (leucine [46], phenylalanine [47], etc.) are also obtained when almost the same sequence of reactions is used:

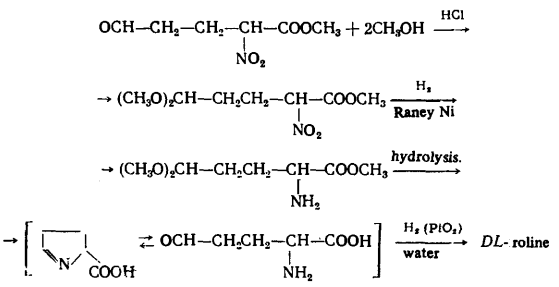
$$R{-}CHO + O_2N{-}CH_2{-}COOCH_3 \rightarrow R{-}\underset{\underset{OH}{|}}{CH}{-}\underset{\underset{NO_2}{|}}{CH}{-}COOCH_3 \xrightarrow{-H_2O}$$
$$\rightarrow R{-}\underset{\underset{NO_2}{|}}{CH}{=}C{-}COOCH_3 \xrightarrow[2)\ \text{hydrolysis}]{1)\ H_2\ (\text{Raney Ni})} R{-}\underset{\underset{NH_2}{|}}{CH_2}{-}CH{-}COOH\,.$$

The addition of methyl nitroacetate to an activated double bond in the presence of bases was proposed as the basis of the synthesis of *DL*-proline [48]:

$$O_2N{-}CH_2COOCH_3 + CH_2{=}CH{-}CHO \rightarrow OCH{-}CH_2CH_2{-}\underset{\underset{NO_2}{|}}{CH}{-}COOCH_3\,.$$

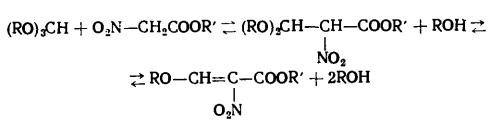
It appeared that when the addition product is hydrogenated over Raney nickel catalyst *DL*-proline is formed, but in low yield and badly contaminated with impurities. This made necessary the preliminary protection of the aldehyde group, which under conditions of reducing alkylation can take part in side-reactions.

The final scheme for making *DL*-proline free from impurities is:

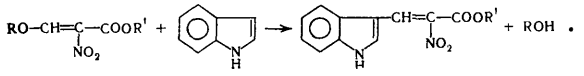


An intermediate in the synthesis of *DL*-proline is Δ^1-pyrrolidonecarboxylic acid which is known to participate in the biosynthesis of proline.

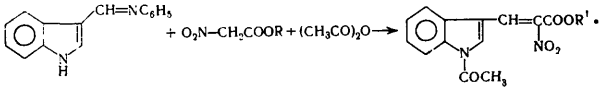
An original method for the synthesis of *DL*-tryptophan was also recently developed[49]. It is based on the condensation of indole with esters of β-alkoxy-substituted α-nitroacrylic acids. The latter is now available and readily obtained by the reaction of a nitroacetic ester with esters of orthoformic acid:



The reaction of indole with α-nitro-β-alkoxyacrylic esters takes place very smoothly and in the absence of catalysts and solvents it leads to an ester of α-nitro-β-(3-indolyl)acrylic acid:

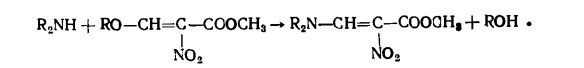


N-Acyl derivative of the same ester was obtained in the reaction of the anil of indolaldehyde with a nitroacetic ester in acetic anhydride[50]:



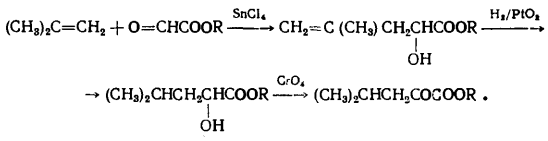
The reduction of both esters and the hydrolysis led to *DL*-tryptophan.

The reaction of α-nitro-β-alkoxyacrylic esters with amines takes place similarly to the reaction with indol[51]. Various substituted esters of β-amino-α-nitroacrylic acid—precursors of αβ-diamino-acids—are formed thereby:



One of the most important diamino-acids—lysine—was obtained by the addition of nitroacetic ester to nitrobutadiene followed by hydrolysis and saponification[52]. The synthesis of *DL*-leucine[53] and *DL*-glutamic acid[54-56] from nitroacetic ester was also described. The path to leucine goes through the alkylation with an alkyl halide, and glutamic acid is obtained after addition to an acrylic ester.

The problem of how much α-amino-acids can be replaced in the diet by the correspondingly constructed α-hydroxy- and α-keto-acids is very interesting. In the last example there is additional interest in that α-keto-acids do not have an asymmetric α-carbon atom. In this connection mention must be made of the interesting synthesis of a keto-analogue of leucine[58,59], by the scheme:



Naturally racemic amino-acids are obtained in the chemical synthesis. The examples of asymmetric synthesis described so far have gone no further than laboratory investigations[57].

The food value of the racemates of amino-acids is naturally lower than that of the natural optically active forms.

The most promising way of resolving the racemates of α-amino-acids is the use of optically active ion-exchange resins, which have become available as the result of investigations conducted in the Institute of Organoelemental Compounds of the Academy of Sciences of the USSR[60]. On the basis of copolymers of styrene with divinylbenzene having a three-dimensional lattice structure of varying density according to the divinylbenzene content, dissymmetric resins containing various optically active compounds (*L*- and *D*- forms of α-amino-acids, their esters and amides, optically active amines, etc.) as ionogenic groupings with an exchange capacity of 3–3.5 mg-equiv. litre^{-1} were synthesised.

On using such exchangers for the resolution of α-amino-acid racemates there is strong enrichment of the eluates by one of the atipodes and in some instances their complete separation[61]. Continuation of the investigations in this direction undoubtedly provides a suitable method of isolating both the *L*- and *D*-isomers of α-amino-acids which gives this method great advantages over others. The *D*-isomers of the *L*-amino-acids thus obtained should find application for carrying out biomedical investigations; after racemisation they can be returned to the separation which allows the total quantity of synthetic α-amino-acids to be used for food purposes.

As regards the analysis of the optical purity of mixtures of amino-acids polarimetric methods are suitable for solving the problems posed by the specific features of the method itself (additivity of total rotation, low sensitivity, and accuracy). It has been shown[62-64] that several compounds which contain asymmetric carbon atoms (amino-acids, hydroxy-acids, alcohols) can be converted into diastereoisomeric esters as a result of the treatment by a corresponding optically active reagent.

The diastereoisomers obtained are chromatographed in the gas phase. This gives a satisfactory separation, both between the stereoisomers and from other substances, including optically active ones. The possibility of a quantitative analysis is determined by the optical purity of the second component used for obtaining the diastereoisomers. Hence it is easy to reach an accuracy exceeding 0.5 rel.% at a sensitivity (in the sense of the possibility of discovering an opposite enantiomer) of 0.2 rel.%[65].

These principles were used in the analysis of protein enzymolysates and hydrolysates. It was shown that the main mass of amino-acids which are present in the enzyme hydrolysate of yeasts are the natural *L*-isomers. The gas chromatographic determination of the ratio of the optical isomers was first used in studying the Akabori reaction. It was found that the copper complex of *L*-alanine reacts with an excess of acetaldehyde and racemic *threo*- and *erythro*-methylthreonines are formed.

The rate of racemisation of the initial substance was less than the rate of formation of the final racemic products. The total experimental results suggested that the reaction proceeds through the copper complex of the imine (Schiff base) which is rapidly racemised by the formation of a carbanion, which reacts with acetaldehyde [41].

4. CHEMISTRY OF ODOUR AND TASTE

The successful progress of the work on the synthesis of food products made it necessary to start investigations of the chemistry of odour and taste in 1963.

Like every purified polymer, the protein constituting the basis of the artificial food has hardly any odour or taste. To make it appetising, it must be given the texture, appearance, flavour, and odour of some particular food product.

The taste of most natural products can be imitated by combinations of four dominating taste sensations, acid, salt, hot, and sweet.† The necessary taste sensations can be matched by combinations of chemicals. The use of natural flavour intensifiers such as sodium *L*-glutamate [69], disodium inosine-5'-monophosphate and disodium guanosine-5'-monophosphate [70] and various others greatly improves the flavour of the product.

The imitation of odour is one of the most complex tasks in the problem of creating synthetic food. Unfortunately it is still impossible to synthesise aromatic compositions with given properties. Attempts to create a theory of odour [71-85] have been made repeatedly [71-85]. That which is best known is the stereochemical theory of Amoore, in which a geometric correspondence of the form and dimensions of the molecules with definite vacancies on the surface of the receptor was postulated. A classification of odours into seven types was proposed: flowery, ethereal, camphor, musky, minty, acrid, and putrid [76,77]. This theory was subjected to thorough criticism [86,87] which was admitted to be correct by Amoore himself, and is now abandoned.

Dyson and Wright's theory [78-82] had many supporters. Wright thought that the sensation of odour arises as a result of vibrational movements proper to the molecules of the odorant and sought to find a correlation between the infrared spectrum of a molecule in the 500–50 cm^{-1} range and its odour. However, under the pressure of the experimental facts Wright admitted that the specificity of the odour could not be connected with the characteristic frequencies of the molecule in the far infrared range [88].

The most promising theory at present is the "membrane puncture" theory developed by Davies and Taylor [83-85] by analogy with the theory of flavour proposed earlier by Beidler [66,89]. According to this theory the corresponding impulse of an olfactory receptor can be the result only of an energetically rich process therefore it is improbable that the primary source of the impulse would be the energy of adsorption or dissolution. The mechanism of the penetration of the odorant to the receptor surface includes the adsorption of the odorant molecule from the mucus surface layer which covers the olfactory surface, then diffusion through the water-mucus layer and adsorption on the surface of the membrane of the olfactory cells, its phosphate-lipid protein layer. The adsorption on the surface of the cell membranes leads to the breakdown of the ordering of its surface layer. This brings about a change in potential existing between the wall of the neurone and the external medium. An ionic current arises because of the transfer of K^+ and Na^+ ions and consequently an electrical impulse, that is, a response to the odorant.

However, this theory is still insufficiently developed for the prediction of odour on the basis of the physicochemical properties of molecules. In connection with this, the starting point in the creation of aromatic compositions is the interpretation of the odour of natural food products [90].

The concentration of odour in a food product is negligible; it usually amounts to a few parts per million, and the number of components often exceeds 200. Therefore an investigation of the nature of odour is unthinkable without specially fine methods of analysis.

In the Institute of Organoelemental Compounds of the Academy of Sciences of the USSR the task was attempted of developing standard free gas chromatographic methods of identifying various classes of organic substances. For this purpose it was necessary to find a relation between the gas-chromatographic behaviour and the structure of the compound. Such a task could be solved only if well reproducible gas-chromatographic parameters existed. The Kovats retention index [91] was first used for the identification of the components of odour; it has good reproducibility [92] and can be used successfully in work on polar stationary phases, even such as ββ'-hydroxypropionitrile [93].

The investigations made showed that there is a marked relation between the index and the structure of the compound investigated, namely the number of carbon atoms, the number of functional groups, and the boiling point. The existence of such regularities gives the possibility of predicting gas chromatographic parameters and consequently of identifying a substance in the absence of a standard.

As an example there is the standard-free method of identifying n-aliphatic amines [94-96], which is now unique in studying the amines in an odour. An analysis of a mixture of primary, secondary, and tertiary aliphatic amines is among the most difficult of gas chromatographic tasks owing to their adsorption on solid carriers and frequent instances of the superposition of chromatographic zones.

This problem was solved by using the known ability of primary and secondary amines to form a hydrogen bond with solid alkali carried on a sorbent [97,98]. The heat of formation of a hydrogen bond found from the chromatographic results and equal for primary amines to $\Delta H = -6.3$ kcal $mole^{-1}$ and the secondary to $\Delta H = -3.6$ kcal $mole^{-1}$ includes a considerable contribution to the value of the index. The retention indices of the tertiary amines on various columns changes slightly.

Further study of the gas chromatographic behaviour of amines allowed a series of equations to be found (Tables 8 and 9) connecting the index with the physicochemical properties of the amines.

Table 9 gives equations for the variation of the index with the boiling point for the primary aliphatic amines. For secondary and tertiary n-aliphatic amines such a relation is observed only on a column with liquid paraffin +2% KOH. The equation has the form $I_{100}^{lp} = 4.0\ (t_k + 85)$ for secondary and $I_{100}^{lp} = 4.0\ (t_k + 79)$ for tertiary amines.

† Apart from the taste sensations listed there are various others, for example, cold, pungent, caustic, metallic, soapy, etc. The existing idea of the presence of only four taste sensations and of four corresponding receptors is inaccurate. In reality each taste receptor has a specific spectrum of responses to tasty substances [66-68].

Optimal conditions were found similarly for the gas chromatographic analysis of mixtures of n-aldehydes, methyl ketones, and α-unsaturated aldehydes[99]. The data needed for the identification are given in Tables 10 and 11.

Table 8. Equations connecting the retention indices with the number of carbon atoms in the molecule of aliphatic amines of normal structure*.

Primary amines, $n \geqslant 2$	Secondary amines, $n \geqslant 4$	Tertiary amines, $n \geqslant 9$
$I^{ts}_{100}=100n+283$	$I^{ts}_{100}=100n+176$	$I^{ts}_{100}=85n+162$
$I^{lp}_{100}=100n+386$	$I^{lp}_{100}=100n+176$	$I^{lp}_{100}=86n+146$
$I^{tw}_{100}=100n+461$	$I^{tw}_{100}=100n+266$	$I^{tw}_{100}=85n+183$
$I^{peg}_{100}=100n+568$	$I^{peg}_{100}=100n+330$	$I^{peg}_{100}=85n+200$

*n is the number of carbon atoms in the amine; I^{ts}_{100}, I^{tw}_{100}, I^{peg}_{100} and I^{lp}_{100} are the indices of the amines at a temperature of 100° in columns with tristearin (ts), Tween 80 (tw), polyethylene glycol-1000 (peg), and 5% liquid paraffin +2%KOH (lp) on "Novator" detergent.

In the general form the scheme of analysis leads to the following: after the concentration of the volatile substances from the food product a definite class of organic compounds is extracted with the aid of chemical reactions. For the gas chromatographic analysis of the mixture of substances of each class a system of three or four columns of different polarity was selected to rule out errors due to the superposition of peaks on the chromatograms. The subsequent identification was made on the basis of the values of the indices and their relation with the number of carbon atoms and boiling point of the test substances.

Table 9. Variation of the retention indices with the boiling point of the amine (t_b).

Equation	Amine	t_b, °C, calculated from I^{ts}_{100}	I^{tw}_{100}	I^{peg}_{100}	t_b, °C (published data)
$I^{ts}_{100}=4.0\ (t_b+91)$	propylamine	54	55	55	45—50
	butylamine	80	80	80	78—79
	pentylamine	104	105	105	104
$I^{peg}_{100}=4.0\ (t_b+116)$	hexylamine	131	130	130	130
	heptylamine	155	155	155	155
$I^{tw}_{100}=4.0\ (t_b+135)$	isopropylamine	35			33—34
	isobutylamine	69			68—69
$I^{peg}_{100}=4.0\ (t+164)$	isopentylamine	96			95
	vinylamine	56			56
	allylamine	54			53

The extract of the odour usually contains many organic substances belonging to different homologous series. In this instance the study of the relation between the index and the structure of the compound assists the identification. The additivity of the contributions reflecting the specific interaction of each functional group with the substrate of the column was established. It appeared that if a substance has several functional groups the total contribution to the value of the index will be equal to the sum of the contributions of all the functional groups. Table 12 gives the equations found for the calculation of the indices of the substances with several functional groups.

Table 10. Equations connecting the retention indices with the number of hydrocarbon atoms in the molecule of monocarboxylic acids*.

Alkanals	2-Alkenals	Methyl ketones
$I^{apm}_{125}=100n+188$	$I^{apm}_{125}=100n+251$	$I^{apm}_{125}=100n+171$
$I^{pega}_{125}=100n+555$	$I^{pega}_{125}=97n+732$	$I^{pega}_{125}=100n+558$
$I^{apm}_{50}=100n+179$	$I^{apm}_{50}=100n+243$	$I^{apm}_{50}=100n+167$
$I^{\beta\beta}_{50}=82n+820$	$I^{\beta\beta'}_{50}=81n+993$	$I^{\beta\beta'}_{50}=81n+856$

*n = number of carbon atoms in the compound; I^{y}_{x}, where x is the temperature of the analysis and y the liquid phase: Apiezon-M (apm), polyethylene glycol adipate (pega), and hydroxydipropionitrile ($\beta\beta'$) on celite.

In an analysis on a polar column the contribution to the index which characterises a functional group rises sharply whereas the contribution introduced by the peculiarities of the structure of the carbon skeleton does not change appreciably. In this connection a very useful quantity for the identification is ΔI, the difference between the indices of a single substance on polar and non-polar columns. ΔI estimates the contribution of a functional group to the value of the index.

Table 11. Variation of the retention indices with the boiling point of monocarboxylic compounds.

Equation	Aldehydes and methyl ketones	Calculated t_b, °C from I^{apm}_{125}	I^{dif*}_{125}	I^{pega}_{125}	I^{apm}_{50}	$I^{\beta\beta'}_{50}$	t_b, °C (published data)
$I^{apm}_{125}=3.8\ (t_b+78)$	C_2-al	24	15	29	24	25	20
$I^{dif}_{125}=3.8\ (t_b+104)$	C_3-al	50	50	49	50.5	51	49.5
	C_4-al	76	75	74	76	75	75.7
$I^{pega}_{125}=3.8\ (t_b+175)$	C_5-al	103	103	103	103	101	103
	C_6-al	129	130	129	130	126	129
$I^{\beta\beta'}_{50}=3.4\ (t_b+260)$	C_7-al	156	157	156	156	151	155
$I^{apm}_{125}=4.2\ (t_b+58)$	C_3-one	57	56	63	52	61	56
$I^{dif}_{125}=4.2\ (t_b+84)$	C_4-one	80	80	83	78	82	79.6
	C_5-one	101	101	102	101.5	101	101
$I^{pega}_{125}=4.2\ (t_b+154)$	C_6-one	127	126	125	128	127	127.5
$I^{apm}_{50}=3.8\ (t_b+74)$	C_7-one	150	150	149	154	152	151.5
$I^{\beta\beta'}_{50}=3.25(t_b+285)$	C_8-one	173	175	173		176	173

*dnp = dinonyl phthalate.

From Table 13, clearly despite the difference in the value of the indices of the substances of normal and isostructure the value of ΔI for a single functional group is almost the same.

A comparison of the results of an analysis on two phases—polar and non-polar immediately gives the possibility of finding a substance with the same functional group.

A knowledge of the functional group in turn allows the number of carbon atoms (n) and boiling point of the compound being determined to be found, by using the appropriate equation.

Table 12. Relation between the retention index and the structure of the substance being analysed.

Equation for variation of the index with the number of carbon atoms $n \geqslant 2$ and the nature of the functional group	Functional group	dI*
For tertiary amines $I_{100}^{peg} = 100\,n + 586$	$-NH_2$	586
For diamines $I_{100}^{peg} = 100\,n + 586.2$		
For secondary amines $I_{100}^{peg} = 100\,n + 330$	>NH	330
For tertiary amines $I_{100}^{peg} = 85\,n + 200$	>N—	200
For alkenes-1 $I_{125}^{apm} = 100\,n - 17$	$>C=CH_2$	−17
For n-alkanals $I_{125}^{apm} = 100\,n + 188$	$-C(=O)H$	188
For ω-alkenals $I_{125}^{apm} = 100\,n - 17 + 188$	$H_2C=C<$ …$-C(=O)H$	
For α-alkenals $I_{125}^{apm} = 100\,n + 251$	$>C=C-C(=O)H$	251
For methyl ketones $I_{125}^{apm} = 100\,n + 171$	>C=O	171
For n-mercaptans $I_{60}^{se**} = 101\,n + 297$	—SH	297
For n-sulphides $I_{60}^{se} = 91\,n + 330$	—S—	330
For n-disulphides $I_{130}^{se} = 93\,n + 546$	—S—S—	546

*∂I is a quantity characterising the interaction of the functional group with the substrate of the column.
** = silicone elastomer SE-30.

Table 13. Quantities ΔI characteristic for n-aliphatic amines.

Amine	$\Delta I^{peg\text{-}tw}$	Amine	$\Delta I^{peg\text{-}tw}$
Methylamine	173	Dimethylamine	90
Ethylamine	111	Diethylamine	63
Propylamine	107	Dipropylamine	60
Butylamine	109	Dibutylamine	62
Pentylamine	105	Dipentylamine	66
Hexylamine	106	Triethylamine	34
Heptylamine	106	Tripropylamine	15
Isopropylamine	100	Tributylamine	16
Isobutylamine	103	Tripentylamine	17

*$\Delta I^{peg\text{-}tw}$ is the difference in the indices of the amine on columns with 10% polyethylene glycol-1000 and Tween-80.

The methods of identification considered above relate to isothermal conditions of analysis. Evidently, the analysis of the components of an odour may sometimes be more convenient by use of gas chromatography with programmed temperature. Therefore attempts were repeatedly made to use isothermal data for identification under conditions of programmed gas chromatographic analysis. A series of empirical formulae was found [100,101].

Recently success was achieved in relating theoretically the isothermal index with parameters which can be determined experimentally [102,103]. A formula was obtained:

$$I_{t_0/\beta} = I_{t_0} + \frac{\beta\tau_x}{2}\frac{\partial I}{\partial t} \qquad (1)$$

in which $I_{t_0/\beta}$ is the index of the test substance with linear programming of the column temperature as a rate β, deg min^{-1}, from an initial temperature of t_0; I_{t_0} the isothermal index at temperature t_0, τ_x the time for the loss of the test substance under the programming conditions, and dI/dt the temperature increment of the index per 1 deg.

Table 14. Composition of monocarboxylic compounds and of volatile components of 5-month Russian cheese.

Aldehyde	Relative %	Aldehyde	Relative %	Ketone	Relative %
Ethanal	5.4	Isopentanal	1.9	Acetone	42.0
Propanal	0.15	Acrylaldehyde	3.3	Butanone	13.7
Butanal	2.0	Pentenal	0.1	Pentanone	5.6
Pentanal	0.7	Butenal	0.17	Hexanone	0.3
Hexanal	0.95	Octenal	0.01	Heptanone	4.6
Heptanal	0.2	Nonenal	0.13	Octanone	0.03
Octanal	0.9	Decenal	0.05	Nonanone	1.6
Nonanal	0.6	2,4-Heptadienal	0.01	Decanone	0.06
Decanal	0.7	2,4-Octadienal	0.04	Undecanone	0.5
Undecanal	0.12	2,4-Nonadienal	0.04		
Isobutanal	0.16				

*A total of 86%; 11 peaks were not identified.

Table 15. Change in the quantitative ratio of volatile amines in Russian cheese on storage, relative %.

Amine	4-months cheese	10-months cheese	Amines	4-months cheese	10-months cheese
Primary			*Tertiary*		
Methylamine	7.4	0.2	Trimethylamine	14.3	3.0
Ethylamine	—	0.3	Triethylamine	4.8	2.8
Propylamine	0.6	—	Tripropylamine	1.2	0.1
Isopropylamine	0.2	0.1	*Heterocyclic*		
Isobutylamine	12.8	0.5	Pyridine	29.6	4.9
Isopentylamine	0.6	0.1	2-Picoline	7.5	52.4
Secondary			3-Picoline	—	0.3
Dimethylamine	2.5	2.5	Piperidine	0.4	15.4
Diethylamine	2.5	1.1	Pyrrolidine	—	0.2
Dipropylamine	2.9	0.5	Hexamethyleneimine	—	0.3
Di-isopropylamine	9.0	8.8			
Dibutylamine	1.2	0.4			
Di-isobutylamine	0.3	0.1			
Unidentified secondary amines	2.3	6.4			

Formula (1) was verified on a large volume of experimental material and allows a substance to be identified in a programmed analysis from the values of isothermal indices.

The methods of identification developed allowed for the first time extremely valuable information to be obtained about the composition of amines and carbonyl compounds in the odours of various natural food products [104-108]. Tables 14–17 give the results.

It is interesting to note that the composition of the volatile components of cheeses have been intensively studied abroad but so far in every instance no more than 11 monocarboxylic compounds were found by gas chromatography [109-111], whereas 30 were identified with the aid of the standard-free method [112].

The use of analytical methods developed in the Institute of Organoelemental Compounds made it possible to establish for the first time that in the volatile components of food products which contain proteins there is a large number of organic bases. Table 15‡ gives the composition of the amines identified in the aroma of 4- and 10-month Russian cheese. During the storage of cheese there is an accumulation of heterocyclic bases. The proportions of some of them were determined by the absolute calibration method (Table 16).

Table 16. Accumulation of amines during storage of Russian cheese.

Substance	Concn. mg per kg cheese	
	4-months	10-months
Piperidine	1.5	50.0
2-Picoline	13.0	80.0
Pyridine	36.0	3.3
Triethylamine	6.0	3.0

The composition of the amines in the volatile components of soft caviar and salmon roes were determined similarly with the aid of standard-free gas chromatography [104,105].

The amines identified are shown in Table 17, which indicates that the relative proportions of the amines is rather specific for each foodstuff. Thus in the volatile components of soft caviar the pyridine content is 21 times that in salmon roe, in which trimethylamine predominates. This shows its organoleptic properties. On the basis of these results an imitation odour was created for synthetic soft caviar. On comparing the composition of the amines in the odour of such varied foodstuffs as caviar and cheese (Tables 15 and 17) the great similarity in the qualitative composition of the amines is seen [106]. This may be because both products contain proteins of animal origin which serve as the precursors of the amines.

The composition of the nitrogenous bases in the volatile components of the foodstuffs is extremely diverse. In addition to the primary amines, secondary and tertiary aliphatic amines are present. The presence of secondary and tertiary amines is somewhat unexpected. It is generally accepted that aliphatic amines are formed in the decarboxylation of amino-acids. However, only primary amines can arise in this manner; secondary and tertiary amines can be formed only as a result of alkylations, which, with the exception of methylation, are unknown. It was interesting to find whether these amines are products of the activity, or arise as a result of decomposition of the organism after the death. For this purpose the composition and kinetics of accumulation of the amines in the volatile components of rapidly growing organisms was studied. The lactic acid bacterium *Streptococcus lactis* was selected as the subject of the investigation.

Table 18 gives the composition of the amines identified in the volatile components of *Streptococcus lactis* at the stage of the logarithmic phase of growth. The organic bases were identified with the aid of the gas chromatographic method of analysis described above.

‡ Under the conditions of the analysis amines appearing on the chromatogram up to n-dodecane were identified.

Table 17. Amines and volatile substances of soft caviar and salmon roes.

Amine	Sturgeon roe, rel. %	Salmon roe, rel. %
Primary		
Methyl-	2.2	3.2
Ethyl-	2.5	—
Propyl-	12.0	—
Isopropyl-	2.0	0.1
Butyl-	3.1	0.3
Isobutyl-	—	1.8
Pentyl-	2.8	0.1
Secondary		
Dimethyl-	2.8	1.0
Diethyl-	2.8	0.4
Dipropyl-	2.6	0.3
Di-isopropyl-	8.6	2.3
Dibutyl-	2.4	0.3
Di-isobutyl	1.8	0.1
Tertiary		
Trimethyl-	3.4	87.5
Triethyl-	9.0	0.3
Tripropyl-	—	0.1
Heterocyclic		
Pyridine	40.4	0.3
2-Picoline	1.4	0.6
Piperidine	—	0.5
Pyrrolidine	—	0.1
	99.8%	99.3%

Table 18. Kinetics of the change in concentration of amines in the volatile substances of lactic acid bacteria.

Amine	Growth of culture, hours		
	6	24	30
Primary			
Methylamine	5.2	0.7	0.1
Ethylamine	0.3	0.1	0.1
Isopropylamine	traces	0.2	0.2
Butylamine	1.5	0.2	0.1
Isobutylamine	0.8	0.7	0.7
Pentylamine	—	0.4	0.4
Isopentylamine	0.7	0.7	0.1
t-Butylamine	1.9	1.3	0.2
Secondary			
Dimethylamine	0.1	1.2	0.1
Diethylamine	2.5	0.5	3.6
Dipropylamine	4.0	1.2	0.7
Di-isopropylamine	9.4	2.8	1.3
Di-isobutylamine	—	1.2	0.6
Butylisopropylamine	15.9	50.6	56.1
Pyrrolidine	2.9	0.4	0.1
Piperidine	5.6	traces	0.1
Unidentified	0.2	0.5	traces
Tertiary			
Trimethylamine	25.7	7.2	2.8
Triethylamine	18.3	2.0	1.7
Tripropylamine	0.7	1.3	0.3
t-Aliphatic amines	4.1	27.0	30.9

As Table 18 shows, the total concentration of amines in the growth of lactic acid bacteria increases, their ratio in the mixture changes sharply, and the concentration of butylisopropylamine and tertiary amines with ten carbon atoms and b.p. 166°C increases [113]. This shows that in the exchange process the bacterial cell secondary and tertiary amines are synthesised, which suggests the existence of specific enzyme systems carrying out the process of synthesis of the amines. Hence a phenomenon

new in principle in biochemistry has been discovered—the synthesis of secondary and tertiary amines by living organisms.

The results of the analysis of the components of the vapour made at the Institute of Organoelemental Compounds of the Academy of Sciences of the USSR shows that under exceptionally thorough work with the aid of gas chromatography it was possible not just to obtain interesting results about the composition of complex aromas of foodstuffs but also to arrive at an understanding of the processes of formation of the food odours. The results obtained show that the problem of odour and taste can be solved successfully. Its solution will enable synthetic foodstuffs to be successful and accepted by people.

5. STRUCTURAL-PHYSICAL PROBLEMS OF ARTIFICIAL FOODS

The production of artificial food requires the solution of yet another great problem—the giving of the usable foodstuffs (of natural, artificial, or synthetic origin) of taste, odour and an attractive appearance. It must be emphasised that each of these factors plays an extremely important part and an underestimate of any of these can lead to the impossibility of admitting and assimilating the food even when its composition is ideal. It is quite evident that an unpleasant or even simply unfamiliar taste of a food provokes in any person an apprehension or even a refusal to use it. The same can naturally be said also about the odour of food.

However, the colour of food and its form are no less serious factors; their being unusual can bring about extremely unpleasant physiological sensations. For example, it was found that artificial soft caviar, the preparation of which was developed in the Institute of Organoelemental Compounds of the Academy of Sciences of the USSR [114-118], having the same composition, structure, and physical properties, exhibiting the same odour and flavour, but differing in colour, aroused greatly differing reactions in a meal. Whereas caviar with the natural colour (greenish grey, dark grey) was regarded as excellent, that coloured bright green was impossible to eat.

Therefore the giving to artificial food of taste and odour and also an attractive appearance was an important problem. It will be examined in greater detail.

It is usually thought that taste is determined by a combination of four sensations, namely, acid, sweet, salt, and hot. However, this is true only in relation to the chemical aspect of taste, since the taste receptors found in the cavity of the mouth actually perceive just these principal taste sensations. Hence this part of the problem of the creation of flavour is readily solved. It is sufficient just to select correctly the ratio of four carriers of these sensations, for example, salt, sugar, any food acid, and coffee.

It is much more difficult to solve another part of the problem of taste having a physical or physicochemical character, which includes above all the creation of a physical structure and definite complex of physical properties for the artificial food.

Actually, the taste sensations in eating are determined not only by the chemical action of the food on the taste receptors but also by the distribution of the sensations of acid, sweet, salt, and hot in relation to individual receptors and also by the mechanical action of the food on the tongue, palate, and teeth, the degree of wetting of the food by the saliva, and by the change in the physical properties of the food–saliva system during its interaction, by bringing about swelling and other physicochemical processes. All this requires a thorough physicochemical investigation of the substances used for preparing artificial foods. Here an investigation of structural and mechanical characteristics is of most value.

Since two of the main ingredients of food—proteins and polysaccharides—are high-molecular-weight substances, the structure-physical task of creating specific forms of artificial food seems [119] part of the general physicochemical problem of creating a desired structure and complex of physical properties for polymeric articles, that is, part of the problem which has occupied investigators working in the field of the physical chemistry of polymers for many years [120].

It must be particularly emphasised that processes of dissolution or dispersion of proteins or polysaccharides, their mixing with one another and with other foodstuffs, odour carriers, dyestuffs, etc. and also the formation of gels from such systems is hindered by a series of problems relating to the physicochemical theory of true and colloidal solutions of polymers. Among such problems there are, for example, the swelling and solubility of food polymers in water, fats and other solvents, the mutual solubility of proteins and polysaccharides, the surface properties of solutions and gels of these polymers, the formation of a structure in solutions of the polymers, the relation between various mechanical properties of the solutions and gels, and their composition and supermolecular structure.

Therefore the whole approach to the modern physicochemistry of polymers can be used for the development of procedures for the production of various forms of artificial food.

The preparation of a specific form of artificial food, for example, caviar, groats, meat, fish, etc. requires, on the one hand, the determination of the complex of structural and physical properties characteristic for the natural product, and on the other hand the development of procedures for the formation of artificial food exhibiting these characteristics. Whereas the first aspect of the problem requires the use of methods of polymer physical chemistry the second aspect seems closely connected with many technological procedures developed in the production of plastics, resins, polymer films, and polymer fibres, adhesives, and lacquers. Actually among foodstuffs there are a series of corresponding forms, namely, homogeneous and heterogeneous, liquid and solid systems (broths, milk, jelly, cheese), layer forms (confectionary), fibrous forms (meat, fish), granular forms (roe, berries, groats), etc. Here the structure can be fine or coarse (porous and frothy foods, emulsions, suspensions, stuffed foods, etc.) and mechanical or other physical properties are extremely varied.

Hence there is a very far-reaching analogy between food and commercial polymer goods allowing the enormous existing experience from the development of various polymers in a variety of articles to be widely used in the creation of one or another form of artificial food. In the development of procedures for the structuring and forming of artificial foodstuffs specific sanitary and hygiene requirements must be borne in mind.

The solution of the problems of artificial food required the development of a large complex of physicochemical investigations of proteins, polysaccharides, and compositions based on them. This is also of general interest for the physical chemistry of polymers. These include, for

example, the investigation of the properties of aqueous and oily solutions and the dispersion of individual food polymers and their mixtures, the study of the effect on these of liquid and gel-forming systems of substances which differ in nature (fats, vitamins, enzymes, sodium chloride, etc.) and also in conditions (temperature and pressure).

To create artificial macaroni and grain articles [121] it is necessary to give them a definite stability of form and volume since on boiling groats or macaroni swelling should occur, but not breakdown of the particles.

Corresponding investigations [122-126] led to the creation of articles of artificial food containing all the necessary nutritive substances (proteins, starch, etc.) with a special space lattice structure. This lattice, completely harmless for the organism, constitutes a negligible part of the mass of the food product but nevertheless gives it elasticity and strength, ensuring the retention of the entity on swelling in boiling water. This naturally gives to the product a certain quality of taste depending on the mechanical properties of the food.

From the physicochemical aspect these investigations led to interesting new results on the physicochemical properties of three-dimensional polymer structures, in particular the properties of the double lattice structures, for example, systems which contain two lattices simultaneously—gelatin and calcium alginate [127].

At present the most far-reaching physicochemical investigations relate to the production of artificial soft caviar. Taking this into account and also the special value of such a delicatessen product this subject will be discussed in greater detail.

In general the preparation of granular forms of artificial food products, for example, artificial groats, berries, roe, etc. leads to the preparation of granules of edible jelly of definite dimensions, chemical composition, and structure, and with the necessary physicochemical properties [128], the creation on these granules of a covering and their colouring the desired shade [123].

In accordance with the process developed for the preparation of artificial caviar various foodstuffs of animal, plant, and microbiological origin and also the products of chemical synthesis can be used. However, at present casein is used as the food raw material; it is a high-quality protein and the problem of its use for feeding is extremely urgent. The essence of the process is as follows. To prepare edible granulated gels, a hot solution of gelatin containing casein or other food substances is supplied dropwise into previously chilled vegetable oil or liquid paraffin.

The resulting granules are kept in the oil at 5–10°C until a gel with a modulus of elasticity of 10^4 dyn cm^{-2} is formed, after which they are separated from the oil and washed with cold water to free the surface from traces of the latter. The formation of gelatin gels is complicated here by the presence of a considerable proportion of casein and other foodstuffs, and also by sorption of oils by the protein components of the gel. Thus, sorption of hydrocarbons by the liquid paraffin leads to a significant change in the melting point, rate of swelling and mechanical properties of the granulated gels. The phase state of the initial mixture of foodstuffs, the conditions of formation, structure, and the corresponding complex of physicochemical properties of granulated gels is determined by the possibility of preparation of a high grade product. To study the effect of these factors on the properties of granulated gels simple and precise methods of determining the temperature range for their fusion, the rates of swelling, and pliability were developed [128] and also a method of investigating the mechanical properties of gels under conditions of uniaxial compression [129,130] and a method of determining the degree of swelling [131] were developed. The possibility of removing oil from the surface of granulated gels when these are washed with water depends significantly on the surface properties of the gel. Gelatin gels are very poorly wetted by water [132]. The introduction of globular proteins into them leads to a distinct change in surface properties, depending on the nature of the protein introduced [133]. The addition of egg albumen is accompanied by some increase in the hydrophobic nature of the gelatin gel, whereas the introduction of even small proportions of casein makes them hydrophilic.

Therefore unlike granules of pure gelatin gel, those of gelatin containing casein are readily washed by water from oil on remixing. The latter treatment of granular gels with aqueous extractants of vegetable tanning agents allows sufficiently definite dense and elastic walls of tanning products to be obtained. The homogeneity of the covering here is determined by the degree of removal of oil from the surface of the granules and by the surface properties of the gel. Aqueous extracts of green tea or the wastes from tea production are used for tanning the granules. [114,123] The colouring of their walls grey-black for the imitating of sturgeon roe is done by treating the granules with solutions of iron(III) salts of bile acids [114,115], that is, by using the well-known reaction of phenolic compounds with iron(III) ions. The properties of the granules are greatly influenced by reagents and media with different osmotic properties applicable for the development of granulated gels (washing, tanning, colouring), and also the conditions of cooking and subsequent storage of the product. The volume properties of the granulated gels do not change appreciably during their tanning. The intensity of the swelling of the gel is depressed in this as a result of the resistance of the granule sheath to extension. The diffusion into the gel of iron(III) ions being used for colouring the sheath is accompanied by the tanning of the proteins through the entire volume of the gel, as a result of which the pliability and intensity of swelling of the gel decrease and its melting point rises.

To make caviar and granules of a gel coated with coloured elastic sheaths, sodium chloride, vegetable oil, fish oil and various other tasty and aromatic substances are added. The combination of casein, vegetable oils, fish oil, and also the additional mineral salt and vitamins introduced weakens the high food values of the product, for the preparation of which high-grade but nevertheless expensive edible raw material was used. In connection with the fact that tea extracts are used for tanning granulated gels their effect has been investigated on the enzyme activity of pepsin, trypsin, and chromotrypsin in vitro [134]. It was shown that the complex of tanning agents of green tea not only does not have an inhibiting action on enzymes under these conditions, but even raises the activity of pepsin and chemotrypsin. Whereas the comparative investigation of the vulnerability of proteins to enzymes of the gastrodigestive tract in vitro and of the same proteins in the composition of various sorts of roe investigated showed that the biological value of these proteins increases on their inclusion in the composition of the product [135]. The investigations of the physicochemical and mechanical properties and also the biological value of the granulated gels allowed the conditions for the preparation of granulated gels to be determined and the influence of various factors on the composition and properties of the prepared product to be characterised, which was a

necessary stage in the development of a method of making artificial soft caviar.

As a result of the studies made in the Institute of Organoelemental Compounds of the Academy of Sciences of the USSR, under the direction of A. N. Nesmeyanov, the first results on the creation of a high quality artificial caviar have been obtained. These studies created the necessary chemical, physicochemical, and technological basis for subsequent development of the investigations in this new and interesting field of science and industry.

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Institute of Organoelemental Compounds,
Academy of Sciences of the USSR

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Study of the Mechanisms of Heterogeneous-catalytic Reactions by the Method of Labelled Molecules (labelled with ^{14}C)

Yu.I.Derbentsev and G.V.Isagulyants

The present review differentiates between the method of labelled atoms (the LA method) and the method of labelled molecules (the LM method). Unlike the LA method, in which an experimental study is made of the distribution of the isotopic tracer over various positions in the molecules of the starting materials and reaction products, the LM method involves the study of the distribution of the isotopic tracer between the molecules of different substances. The basic equations of the LM method for integral and differential reactors are given, and literature on the application of the LM method with the ^{14}C isotope to study the mechanisms of heterogeneous-catalytic reactions is reviewed. The bibliography contains 163 references.

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1. INTRODUCTION

At the present time there are two main ways in which isotopes are used to study the mechanisms of catalytic reactions. In the first, it is possible to follow experimentally the distribution of the isotopic tracer in various positions in the molecules of the starting materials and reaction products, and this in turn makes it possible to obtain information on the relative reactivity of the atoms in the positions selected, on the course of the reaction, etc. This method could be called the labelled atom method in the narrow sense (the LA method).

In the second, we follow the distribution of the isotope not inside the molecules, but between the molecules of different substances or, as for example in the isotopic differential method for studying the surface of catalysts, between different parts of molecules of the same substance. This makes it possible to determine the role of the labelled substance in a multi-stage catalytic process, and to study the properties of the catalyst and the nature of the products of its interaction with the reacting molecules. This method might be called the labelled molecule method (the LM method).

The LM method can be used to study a wider range of specific problems in heterogeneous catalysis than is possible by the LA method. It need only be pointed out that this method has been used to study inhomogeneity (see for example Refs. 1–3), acid–base properties[4], surface area[5,6], the poisoning of catalysts[7], the interaction of adsorbed substances on a surface[8–10], the kinetics of heterogeneous-catalytic reactions[11–15], etc. Many theoretical aspects of the use of isotopes in catalysis were examined in detail in a monograph by Roginskii[16] and to a lesser extent in other monographs (see for example Refs. 17–19). A brief review by Trimm[20] was devoted to the use of carbon isotopes to study neterogeneous catalysis.

At the present time, nowever, there is no sufficiently complete review of work carried out by the LM method in various fields of heterogeneous catalysis, and in the study of the mechanisms of the reactions in particular. The aim of the present work is to fill this gap.

2. POSSIBILITIES OF THE LM METHOD IN THE STUDY OF THE MECHANISMS OF CATALYTIC REACTIONS

A particular example of the method of "labelled molecules" is provided by the analytical method of isotopic dilution[21,22], which makes it possible to determine extremely small quantities of substance when radioactive tracers are used; it is better to have the tracer in the substance being determined then to have it in the diluent. An example of the use of this method for the analysis of the products of a heterogeneous-catalytic reaction was described by Blau and Willard[23], who studied the reaction of benzene-^{14}C and ethyl chloride vapours over solid aluminium chloride (sublimed on the walls of the flask) at room temperature. The reaction products, obtained in small quantities, were diluted with a measured amount of unlabelled benzene, ethylbenzene, and diethylbenzene, after which the mixture was fractionated and the yields of the corresponding products were determined from the specific radioactivity of the components. In this work it was possible to show that the rate of formation of ethylbenzene depends on the pressures of both starting materials.

The method of isotopic dilution as such apparently will not be very important for the study of organic reactions, since the development of chromatography has given research workers more convenient and sufficiently sensitive methods of analysis. The determination of specific radioactivity is widely used, however, in other isotopic methods for studying reaction mechanisms, in particular in the kinetic isotopic method, which makes it possible to determine quantitatively the rates of formation and consumption in given directions for a given substance in a reacting system, and this helps to establish a scheme of genetic relationships for the products.

As early as 1937, Wilson and Dickinson[24] showed that for the reversible redox reaction

$$H_3A^{V}O_3 + I_3^{-} + H_2O \rightleftarrows H_3AsO_4 + 3I^{-} + 2H^{+} \quad (1)$$

it is possible, by using radioactive tervalent arsenic, to study the rates of the forward and back reactions at equilibrium by making use of the equation

$$\frac{d\alpha}{dt} = \frac{R}{[As^{V}]}(\beta - \alpha) \quad (2)$$

where α is the specific radioactivity of H_3AsO_4; β the specific radioactivity of H_3AsO_3; R the reaction rate; and $[As^{V}]$ the concentration of H_3AsO_4 (assumed constant). To calculate R, Wilson and Dickinson[24] used the integral form of this equation.

The kinetic features of biochemical processes have been studied with labelled substances by Zilversmit[25], Barnum and Huseby[26], and others. A review of work by non-Soviet authors in this field is given in Aronoff's monograph[27].

Neiman[28-30] gave the derivation of the equation

$$\frac{d\alpha}{dt} = \frac{w(\beta - \alpha)}{[X]} \quad (3)$$

where w is the rate of formation of the product from a single radioactive precursor; [X] the concentration of the product X; β the specific radioactivity of the precursor; and α the specific radioactivity of the product, and used it to find the rates of the formation and decomposition of the intermediate products; he called this method the kinetic isotopic method (KIM) for studying reaction mechanisms.

Eqn. (3) can be written for the general case of the formation of a substance X from any number of radioactive precursors[31]:

$$\frac{d\alpha_X}{dt} = \frac{1}{n[X]}\sum_{i=0}^{i} w_i(\alpha_i - \alpha_X) \quad (4)$$

where w_i is the rate of the process i leading to the formation of the substance X; α_i the specific radioactivity of the corresponding precursor; α_X the specific radioactivity of the substance X; [X] the concentration of the substance X, %; and n the total number of moles of the substance in the system. The overall equation of the material balance for X can evidently be written in the form

$$\frac{dn[X]}{dt} = \sum_{i=0}^{i} w_i - \sum_{j=0}^{j} w_j \quad (5)$$

where w_j is the rate of consumption of the substance X.

In integral form and applied to the conditions of heterogeneous catalysis, Eqns. (4) and (5) are written in the form

$$\frac{\alpha_X - \alpha_{X_0}}{st} = \frac{1}{n_0[X]_0}\sum_{i=0}^{i} w_i(\alpha_i - \alpha_X) \quad \text{or}$$
$$\frac{\alpha_X - \alpha_{X_0}}{s} = \frac{1}{u[X]_0}\sum_{i=0}^{i} w_i(\alpha_i - \alpha_X) \quad (6)$$

and

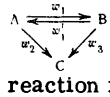
$$\frac{n_0\{[X] - [X]_0\}}{st} = \sum_{i=0}^{i} w_i - \sum_{j=0}^{j} w_j \quad \text{or} \quad \frac{u\{[X] - [X]_0\}}{s} = \sum_{i=0}^{i} w_i - \sum_{j=0}^{j} w_j \quad (7)$$

where α_{X_0} is the specific radioactivity of the substance X in the original mixture; n_0 the number of moles of the starting material; $[X]_0$ the percentage concentration of the substance X in the original mixture; [X] the same in the reaction products; s the catalyst surface area; and u the rate of supply of the starting material ($u = n_0/t$).

Eqns. (4) and (5) [or (6) and (7) respectively] are the most general equations of the kinetic isotopic method, and they make it possible to find the rates of formation and consumption of a substance in complicated reactions.

In the study of genetic relationships and in the verification of stepwise schemes, the first problem which arises concerns the extent to which a product B, formed from the starting material A, takes part in the formation of the final product C.

To solve these problems, Balandin and coworkers[32,33], beginning in 1958, used the triangular scheme



(8)

The equations for the reaction rates in this system can readily be obtained from a system of equations of types (4) and (5) or (6) and (7) respectively.

Differential reactor

$$w_1 = \frac{u[B_0](\alpha_{B_0} - \alpha_B)}{s(\alpha_B - \alpha_A)} \quad (9)$$

$$w_1' = \frac{u[A_0](\alpha_{A_0} - \alpha_A)}{s(\alpha_A - \alpha_B)} \quad (10)$$

$$w_2 = \frac{u\{[C] - [C_0]\}}{s} - w_3 \quad (11)$$

$$w_3 = \frac{u\{[C](\alpha_C - \alpha_A) + [C_0](\alpha_A - \alpha_{C_0})\}}{s(\alpha_B - \alpha_A)} \quad (12)$$

Integral reactor

$$w_1 = \frac{d\beta}{d\tau}\frac{[B]n}{(\alpha_A - \alpha_B)} \quad (13)$$

$$w_1' = \frac{d\alpha}{d\tau}\frac{[A]n}{(\alpha_B - \alpha_A)} \quad (14)$$

$$w_2 = \frac{dn[C]}{d\tau} - w_3 \quad (15)$$

$$w_3 = \frac{\frac{d\alpha_C}{d\tau}n[C] + \frac{dn[C]}{d\tau}(\alpha_C - \alpha_A)}{\alpha_B - \alpha_A} \quad (16)$$

The significance of the symbols in Eqns. (9)–(16) is clear from the foregoing.

It is obvious that when $w_3 = 0$, B and C are formed by parallel independent paths. When $w_2 = 0$, the formation of the product C is a purely consecutive process. In this case the rate w_3 can be found from Eqn. (3)

$$w_3 = \frac{d\gamma}{d\tau}\cdot\frac{[C_3]}{\beta - \gamma} \quad (17)$$

or

$$w_3(\beta - \gamma) = [C_3]\cdot\frac{d\gamma}{d\tau} \quad (18)$$

Eqn. (18) has important consequences:

$$\text{for } \frac{d\gamma}{d\tau} > 0, \quad \beta > \gamma \quad (19)$$

and

$$\text{for } \frac{d\gamma}{d\tau} < 0, \quad \beta < \gamma \quad (20)$$

The inequalities (19) and (20) are necessary but not sufficient conditions for formation of the product C from a single precursor B. Although these conditions follow from the equations of the kinetic isotopic method, they are of independent importance, and, as shown below, they are used more widely than the other equations of the method.

Hightower and Emmett[34], in a study of the cracking of cetane, expressed the fraction of the consecutive path for the formation of the product i through the product a in the form of the ratio

$$\alpha_a^i(\text{obs})/\alpha_a^i(\text{max})n \qquad (21)$$

where α_a^i (obs) is the experimental value of the ratio of the specific radioactivities of the product i and the product a in the catalysate, α_a^i (max) the calculated maximal value of this ratio, and n the number of moles of substance a required for the formation of one mole of substance i. Assuming that the consecutive reactions in this instance are of first order, the authors cited find that the value of α_a^i (max) lies in the range 1–3.

A number of authors (see for example Refs. 35 and 36), in experiments with mixtures containing a labelled substance, calculate the so-called intensities of the reaction, by which is meant the yields of the products separately from each component of the original mixture. The ratio of the intensities indicates the relative reactivity of the substances when present together in the reaction zone, and can be used to obtain information on the reaction mechanism; the ratio of the intensities, however, unlike the ratio of the rates of the processes, does not contain information on the reaction paths, and in most instances it does not make it possible to obtain unambiguous information on the adequacy of the proposed and real sequence of processes.

In concluding this section we may point out that the LM method is fundamentally related to the analytical method of radiochromatography, which makes it possible to carry out the simultaneous chemical and radiometric analysis of complex mixtures of substances.

The high efficiency of this method makes it possible in turn to use micro-catalytic apparatus to carry out experiments, and this is extremely convenient from the safety viewpoint and in connection with the use of expensive radioactive materials. The foundations of the application of radiochromatography combined with micro-catalytic apparatus were laid by Emmett and coworkers[37], and in the Soviet Union the use of radiochromatography in catalysis was pioneered by Roginskii and Yanovskii and coworkers[38–40].

3. DETERMINATION OF THE STOICHIOMETRIC NUMBER

The stoichiometric number of a reaction characterises the reaction mechanism[41]. The stoichiometric number γ can be determined experimentally if the rates of the forward and back reactions are measured under the same conditions

$$\gamma = \frac{-\Delta G/RT}{\ln \frac{v_+}{v_-}} \qquad (22)$$

where ΔG is the Gibbs free energy under the conditions of the reaction; R the gas constant; T the absolute temperature; v_+ the rate of the forward reaction; and v_- the rate of the back reaction.

When isotopes are used to determine the forward and back reaction rates, a reasonable integral value of the stoichiometric number can be expected only if the isotope takes part in the limiting stage of the reaction. Thus to determine precisely the limiting stage it is best to determine the stoichiometric number by means of various isotopes. Using ^{14}C, Kaneko and Oki[42] determined the forward and back reaction rates for the conversion of water gas:

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (23)$$

in the presence of iron(III) oxide, and this enabled them to determine γ, which was found to be equal to 1. After examining three possible mechanisms:

$$\left.\begin{array}{l} H_2O \rightarrow 2H\,(a) + O\,(a) \\ CO + O\,(a) \rightarrow CO_2 \\ 2H\,(a) \rightarrow H_2 \end{array}\right\} \qquad (24)$$

$$\left.\begin{array}{l} H_2O \rightarrow H_2O\,(a) \\ CO \rightarrow CO\,(a) \\ H_2O\,(a) + CO\,(a) \rightarrow H_2 + CO_2 \end{array}\right\} \qquad (25)$$

$$\left.\begin{array}{l} H_2O \rightarrow H_2O\,(a) \\ H_2O\,(a) + CO \rightarrow H_2 + CO_2 \end{array}\right\} \qquad (26)$$

where (a) denotes the adsorbed state, and pointing out that according to published data[43] the value of γ determined by means of deuterium is also equal to 1, the authors cited rejected mechanism (24), since it does not contain a stage in which carbon and hydrogen atoms take place simultaneously, and concluded that the mechanism operating is either (25) or (26).

In analogous studies, Atkins and Happel[44] used ^{14}C to determine the stoichiometric number for the dehydrogenation of butane

$$C_4H_{10} \rightleftarrows C_4H_8 + H_2 \ . \qquad (27)$$

In this instance also, γ was found to be equal to 1. From this it follows that the adsorption or desorption of hydrogen cannot be the limiting stage of the reaction; a limiting stage, if one exists, can only be a stage in which transformation of the carbon framework of the molecule takes place. Atkins and Happel[44] assume that the reaction has not one but several limiting stages, the stoichiometric number of each being equal to unity.

4. PROBLEM OF THE ISOTOPIC EXCHANGE OF CARBON

For the interpretation of the results obtained by the labelled molecule method, it is important that intermolecular isotopic exchange of carbon in the organic compounds is unlikely under the usual conditions in which catalytic reactions are carried out. In a number of studies the possibility of exchange has been verified experimentally.

For example, Emmett and coworkers[45] showed that methane, n-butane, and acetylene under the conditions of the Fischer–Tropsch synthesis remain almost non-radioactive after contact with labelled carbon deposited on the catalysts: appreciable transfer of radioactivity (2%) was observed only for but-1-ene. Under the severe conditions of cracking over an aluminosilicate catalyst (500°) the transfer of radioactivity between ethane and propane, and between methane and ethylene, amounted to fractions of 1%[46]; there was almost no transfer of radioactivity between methane and carbon. In the interpretation of the results obtained, it must of course be borne in mind that the transfer of radioactivity from one product to another (in the works cited) does not in itself prove that exchange

takes place, if the back reaction has not been studied experimentally. It is quite probable that labelled compounds took part in the synthesis of those substances in which the radioactivity was determined.

In this connection, mention must be made of the so-called isotopic-radical exchange of carbon. Vasserberg and coworkers [47-49] found that when substances containing radiocarbon, for example $^{14}CH_3OH$ (called the "tracer donor") are passed over alumina together with an unlabelled oxygen-containing compound, for example ethanol (called the "tracer acceptor"), the products of the transformation of the latter (in this instance ethylene) were found to contain a small amount of radioactivity. This led to the development of the idea that exchange of carbon takes place between methanol and ethanol and also between other compounds as a result of the reaction of intermediate radical-like formations on the surface of the alumina.

These observations attracted some attention [50], but it was later shown [51,52] that under the conditions of dehydration on alumina, methanol gave small quantities of ethylene and propene, and ethanol gave propene. The addition of non-radioactive ethanol to radioactive methanol does not increase the formation of radioactive ethylene. It is evident that in the interpretation of the results of this work [47-49] we may be dealing not with the exchange of carbon but with side reactions involving the transformation of the tracer donor. The use of the acceptor merely facilitated the detection of small quantities of these side products.

It may thus be concluded that at present there is no evidence of the possibility of heterogeneous-catalytic exchange of carbon in organic compounds.

5. CATALYTIC CRACKING OF HYDROCARBONS

First in Roginskii's laboratory, and subsequently in work by Emmett and coworkers, it was shown that in the cracking of hydrocarbons, alkenes with lower molecular weight are the primary reaction products; the addition of ethylene-^{14}C to n-hexane [53], propene-^{14}C to 2,2,4-trimethylpentane [53], and propene-^{14}C, pent-1-ene-^{14}C, and hept-1-ene-^{14}C to n-hexadecane [34,54,55] over aluminosilicate catalysts under the conditions of cracking led to the formation of products whose specific radioactivity was close to or greater than that of the added labelled substance in the catalysate.

The addition of labelled alkanes to the starting materials in the cracking usually did not lead to the formation of hydrocarbons with appreciable radioactivity [34,53-55]. An exception is provided by work [56] in which labelled ethane mixed with n-octane at 500° over an aluminosilicate was dehydrogenated with the formation of ethylene.

These results show good agreement with the idea that cracking takes place by an ionic mechanism. In agreement with the fact that primary carbonium ions require more energy for their formation than secondary carbonium ions, ethylene takes a smaller part in the formation of the final products compared with other alkenes used as labelled additives to alkanes [34,53,55]. It should be noted, however, that the labelled compounds added to alkanes during cracking influence the reactivities of the original hydrocarbons.

It has been found [53] that labelled ethylene added to 2,2,4-trimethylpentane and propene under the conditions of cracking over an aluminosilicate takes part in the formation of products with the C_3 and C_4 compositions; in the experiments in which labelled ethane was added to 2,2,4-trimethylpentane, an even greater interaction was observed. In the opinion of the authors cited, these changes are due to degradative alkylation, taking place with the formation of intermediate bimolecular complexes, for example:

$$^{14}C_2H_6 + C_3H_8 \rightarrow (^{14}C_2H_6 \cdot C_3H_8) \begin{matrix} \nearrow {}^{14}C_4H_8 + CH_4 \\ \searrow C_4H_8 + {}^{14}CH_4 \end{matrix} . \qquad (28)$$

It is possible that in these processes a definite part is played by the recently discovered reaction of alkene disproportionation. It has been suggested [57,58] that this reaction involves the intermediate formation of a bimolecular complex with a four-membered ring structure:

$$\begin{matrix} R_1{-}CH{=}CH_2 \\ +CH_2{=}CH{-}R_2 \end{matrix} \rightarrow \begin{matrix} R{-}CH \cdots \vdots \cdot CH_2 \\ H_2C \cdots \vdots \cdot CH{-}R_2 \end{matrix} \rightarrow \begin{matrix} R_1{-}CH & CH_2 \\ \| & + \| \\ CH_2 & CH + R_2 \end{matrix} . \qquad (29)$$

Andrianova and Roginskii [56,59] showed that the addition of small quantities of alkenes (up to 2.5%) increases the extent of the cracking of n-octane, whereas an increase in the quantity of additive decreases the rate of cracking. The addition of alcohols has a similar influence, and this, in the opinion of the authors cited, is due to the formation of alkenes from the alcohols under the conditions of the reaction. They suggested that the cracking reactions take place by a chain mechanism, and that small quantities of alkenes initiate the process, whereas large quantities suppress it.

It might be expected that aromatic hydrocarbons would also take part in alkylation in the same way as alkenes, but the experiments of Hightower and Emmett [34,55] with the addition of labelled benzene and toluene to n-hexadecane under the conditions of cracking over an aluminosilicate catalyst showed that when these hydrocarbons are used, only a small proportion of alkylaromatic compounds are obtained. These are obtained chiefly from the products of the cracking of n-hexadecane as a result of the polymerisation and copolymerisation of alkenes with three or more carbon atoms in the molecule.

The use of labelled mixtures of alkanes and alkenes established that under the conditions of cracking, the carbonaceous deposits on the catalyst are also obtained chiefly from the alkenes [53,54,56,59,70]; with increase in the molecular weight of the alkane, the extent to which it takes part in the formation of carbon increases [59,61].

To study the problem of whether carbon is obtained by the gradual loss of hydrogen atoms or by the removal of terminal carbon atoms from the hydrocarbon molecules, McMahon [62] determined the specific radioactivity of the carbon after passing n-heptane-4-^{14}C, n-octane-1-^{14}C, and oct-1-ene-1-^{14}C over a catalyst. In all instances the specific radioactivities of the starting material and the carbon were equal, providing evidence in support of the first hypothesis. In Wynnemer's experiments [63], however, the specific radioactivities of carbon deposits obtained at 454° and 510° from the same substance (n-decane-2-^{14}C) were different, indicating that the mechanism of carbon formation may depend on the temperature.

6. OXIDATION OF HYDROCARBONS

The mechanism of the extensive oxidation of alkenes has been studied by Neiman's method, chiefly by Margolis and coworkers in Roginskii's laboratory; this work has been reviewed in sufficient detail [64,65] and we shall give only a brief description here. A series of experiments were undertaken to observe the reaction sequence: alkene → product of incomplete oxidation → carbon dioxide,

which might indicate the primary product of the oxidation of the alkene. Oxides of hydrocarbons, aldehydes, and other compounds were considered as possible primary products. It was shown that over a silver catalyst, ethylene is oxidised to carbon dioxide by a parallel-consecutive mechanism—through the intermediate formation of ethylene oxide and also directly[66-68]. Formaldehyde and acetaldehyde decreased the rate of oxidation, so that they could not be intermediate products[67,68]. Ethylene oxide and acetaldehyde added to ethylene over vanadium oxide took an active part in the formation of carbon monoxide and dioxide, but since almost no ethylene oxide and acetaldehyde are detected in the oxidation of ethylene, the authors cited[69,70] concluded that ethylene is for the most part oxidised directly to carbon dioxide.

In studies of the oxidation of propene on copper catalysts, it was established that carbon dioxide is formed by a parallel-consecutive mechanism with the participation of acrolein formed as an intermediate[71,72].

It has also been shown[69,70] that aldehydes take an active part in the formation of the carbonaceous film on the catalyst, and that this has some influence on the selectivity of the oxidation processes.

Radiocarbon ^{14}C has also been used to study the mechanism of the extensive oxidation of toluene over a copper catalyst[73]. In experiments in which labelled benzyl alcohol and benzaldehyde were added to toluene, the authors cited concluded that toluene is oxidised to carbon dioxide partly through the intermediate formation of benzyl alcohol. Unfortunately, the results of this work are not reported in sufficient detail.

7. SYNTHESIS OF HYDROCARBONS AND ALCOHOLS FROM CARBON DIOXIDE AND HYDROGEN

Radiocarbon ^{14}C has been used in a large number of studies to investigate the problems of the mechanism of the synthesis of hydrocarbons and alcohols from CO and hydrogen. Most of this work was recently reviewed by Eidus[74], and we shall here list only the main features and the results obtained in this work.

Emmett and coworkers[45] used catalysts carbonised in the presence of radioactive carbon monoxide, and found that the radioactivity is transferred to the products of the synthesis to only a slight extent; this proved that surface metal carbides are not intermediate products of the synthesis. Subsequently, similar results were obtained in other studies over cobalt[75] and iron[76,77] catalysts. It is now generally accepted that some surface complexes involving CO and H_2 must be formed during the reaction to act as intermediate link. Ganguli[78], in a study of the simultaneous adsorption of CO and H_2 on a cobalt catalyst, showed that whereas exchange of the adsorption complex with gaseous CO takes place to a slight extent, the reaction products contain appreciable radioactivity; this proves that the CO–H_2 complex take part in the synthesis. In a large number of studies, various labelled substances have been added to the gas taken for the synthesis, in order to detect intermediate compounds. Examination of the published material shows that all the radioactive additives used can be divided into three groups according to the nature of their participation in the synthesis. The first group contains substances capable of generating radioactive carbon monoxide—methanol[79-81], formaldehyde[80], methyl formate[82], and keten[83] labelled in the carbonyl group. A characteristic feature of this group of substances is that in their presence, the molar radioactivity of the products increases with increase in molecular weight, and this can be regarded as confirming their role as the source of radioactive carbon monoxide, which is the chief "building material" in the synthesis.

The second group contains labelled substances whose addition leads to the formation of hydrocarbons with constant molar radioactivity—ethylene[77,84-86], ethanol[82,87-91], n-propanol[79-81], acetaldehyde[82], propionaldehyde[85], and keten labelled in the methylene group[92]. These substances are apparently capable of generating methylene radicals, which can initiate the synthesis[93].

In a study of the addition of ethanol to the gas taken for the synthesis[87,90,91], it was shown by the LA method that C_3 hydrocarbons are obtained by the attachment of a new carbon atom to the carbonyl carbon atom of the alcohol. Added aldehydes under the conditions of the synthesis are apparently readily hydrogenated with the formation of alcohols[82], and this explains the similarity in the behaviour of aldehydes and alcohols. It should be noted, however, that over a fused iron catalyst, added acetaldehyde was converted into higher alcohols more rapidly than added ethanol, by a factor of several orders of magnitude[94].

The third group contains substances which take little part in the synthesis (propene[75], butenes[95], isopropyl alcohol, and n-butanol[79-81]), and also methane[96,97] and carbon dioxide[80] which take almost no part in the synthesis.

Among the substances added to the gas taken for the synthesis, a unique position is occupied by ethylene. Fletcher and Gibson[98] showed that a mixture of hydrogen and ethylene in the presence of a small quantity (5%) of ^{14}CO gave hydrocarbons whose specific radioactivity was several times smaller than that of the original carbon monoxide; the low radioactivity of methane and the absence of any periodicity in the radioactive higher hydrocarbons with even and odd numbers of carbon atoms suggested that during the synthesis, ethylene is first dissociated to methylene radicals. When large quantities were added, it was found that ethylene takes part not only in the initiation of the synthesis but also in the growth of the hydrocarbon chains[75]. In recent years, the hydropolymerisation of ethylene in the presence of small quantities of CO over a cobalt catalyst has acquired independent interest. It has been shown[99] that the quantity of CO in the mixture remains almost unchanged during the experiment, whereas the process does not take place without CO. It might be suggested, however, that the maintenance of the CO concentration is due to the attainment of equilibrium in reactions involving its consumption and formation. This possibility was examined[100] by means of labelled CO and it was found that under certain conditions its specific radioactivity remains unchanged, so that CO is not formed during the synthesis, whereas ethylene is used up intensively in the reaction; it was thus proved that CO under these conditions acts as reaction initiator.

Radiochromatographic analysis has indicated that the highest radioactivity is shown by α-alkenes and the corresponding alkanes; β-alkenes, among which the cis-isomers predominated, showed a lower radioactivity, so that they were obtained by a different mechanism, and were not produced from the α-alkenes by isomerisation. An interesting feature is that in this work, although ^{14}CO was only the reaction initiator, an increase in the molar radioactivity of the hydrocarbons with increase in molecular weight was observed. A possible explanation is that with increase in the length of the chain there is an increase in the probability of a type of hydrocarbon desorption in which the primary complex on the surface decomposes and

the radioactive carbon is introduced into the molecule; it is suggested that most of the hydrocarbon molecules are desorbed in a different way, without decomposition of the primary complex.

It is also interesting to note that under the conditions of the synthesis of alcohols with the addition of labelled ethylene to the gas taken for the synthesis, propanol with a high specific radioactivity was obtained [86,101], and this has made it possible to come closer to the development of conditions for the preparation of propanol from ethylene, carbon monoxide, and hydrogen [86].

8. SYNTHESIS OF BIVINYL FROM ALCOHOL

^{14}C has been used to study the mechanism of the formation of bivinyl from alcohol on Lebedev's catalyst. It has been shown that ethylene and ether are not intermediate products [102,103], and that methanol takes part only in the formation of side products of the synthesis of bivinyl [104,105]. On the other hand, the addition of labelled crotonaldehyde to the original alcohol led to the formation of highly radioactive bivinyl [102,103]. Although crotonaldehyde was not detected in the condensates under the conditions of the experiments, so that the specific radioactivities of these products could not be compared, the results can be taken as confirming Gorin's familiar scheme [106], in which crotonaldehyde takes part as an intermediate product.

When labelled acetaldehyde was added to the alcohol, it was established that these substances in the mixture are readily interconverted [102,103]:

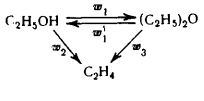
$$^{*}C_2H_5OH + CH_3CHO \rightleftarrows C_2H_5OH + {}^{*}CH_3CHO. \qquad (30)$$

Because of this, the part played by acetaldehyde in the synthesis of bivinyl could not be determined by this method. A radiochromatographic study [38] established that the formation of butenes takes place not as a result of the hydrogenation of bivinyl but by the dehydration of butanol produced in the reaction. The use of ^{14}C also showed that under the conditions of the synthesis of bivinyl by Lebedev's method the formation of carbonaceous deposits on the catalyst takes place chiefly from the original alcohol, and not from the bivinyl [107]. It may also be noted that in the dehydration of alcohol over titanium dioxide the carbonaceous film is again formed chiefly from the alcohol, and not from the alkene [108]; in the decomposition of alcohol over a dehydrogenating catalyst (copper on silica gel), the carbonaceous film was obtained chiefly from the acetaldehyde [109].

9. DEHYDRATION OF ALCOHOLS AND ACCOMPANYING REACTIONS

^{14}C has been used to make detailed studies of various problems of the mechanism of the dehydration of alcohols. Thus a discussion has been going on for a long time in the literature on the mechanism of formation of ethylene in the dehydration of ethanol over alumina.

Some authors consider that the formation of the alkene takes place by consecutive reactions, and that ether is first formed as an intermediate product. Others consider that ethylene and ether are formed by two independent parallel reactions. In 1958, a parallel-consecutive scheme was proposed for the dehydration of ethanol:



(31)

and the rates of the separate processes were determined experimentally [32,110]. For this purpose the dehydration of ethanol was studied with the addition of ^{14}C-labelled diethyl ether, at 275, 300, 350, and 400° in a flow reactor over industrial alumina.

It was found that at 275°, ethylene is formed directly from the alcohol and with the intermediate formation of ether at approximately equal rates; with increase in temperature the direct formation of ethylene from alcohol predominates. Thus on alumina, direct decomposition of alcohol to ethylene and water is possible; the bimolecular dehydration with the formation of ether and water takes place independently, but the ether formed is unstable under the conditions of the reaction and is itself able to undergo dehydration with the formation of ethylene and water. The mechanism of the dehydration of alcohol on an aluminosilicate catalyst is analogous [111].

In connection with the suggestion that the formation of ether and ethylene takes place through a common surface intermediate compound, which is present in equilibrium with the alcohol and ether [112,113], the method of isotopic dilution was used to study the chemosorption of mixtures of alcohol and ether on alumina at 120°; transfer of the radioactive tracer between the alcohol and the ether was not observed, so that, at low temperatures at least, there is a difference between the surface compounds formed from alcohol and ether [10].

Unlike alumina, a number of other oxides bring about not only dehydration but also dehydrogenation of alcohols with the formation of aldehydes or ketones. Saturated hydrocarbons are often detected in the catalysate gas together with unsaturated hydrocarbons and hydrogen. It is often assumed that the saturated hydrocarbons are formed by hydrogenation of an alkene. A number of authors, however, have pointed out the possibility of hydrogenolysis of alcohols at the C–C bond under the conditions of the reaction, since the catalysates were found to contain alkanes with one carbon atom less than the original alcohol [114,115]; in this connection it was suggested that alkanes may also be formed by the hydrogenolysis of alcohol at the C–O bond [116].

Experiments in which ethanol containing labelled ethylene was passed over titanium dioxide [108] and in which isopropyl alcohol with added propene was passed over vanadium(III) oxide [116] showed that the radioactive tracer was not converted into ethane and propane respectively, and was not detected in the liquid catalysates. These experiments confirmed that under the conditions of dehydration the alkanes are probably produced by the hydrogenolysis of alcohols, and not by hydrogenation of alkenes liberated into the gaseous phase.

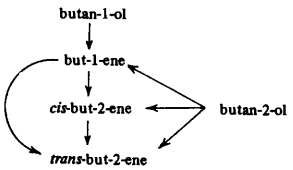
The isotopic-kinetic method has also been used to study the genetic relationships between the products in the more complex system formed in the dehydration of butanols.

The aim of the study was to follow the change in the ratio of the rates of the dehydration of alcohols and the isomerisation of the resulting butenes, and also to determine the reasons for the frequently observed preferential formation of but-1-ene and *cis*-but-2-ene from secondary butyl alcohol, which cannot be explained on the basis of a mechanism of dehydration involving a classical carbonium ion and for which the concept of a π-complex has been introduced [117] or for which it has been suggested that but-1-ene is an intermediate product of the formation of but-2-ene from butan-2-ol [118].

The studies were carried out over two specimens of alumina: grade A-1 [119] and industrial fluorinated grade [120]. These catalysts differ in their isomerising properties.

^{14}C-labelled butan-1-ol was added to the butan-2-ol to act as a source of labelled but-1-ene (it should be noted that in this instance the labelled hypothetical intermediate compound was not introduced in prepared form into the reaction zone but was synthesised during the reaction on the surface of the catalyst).

The reaction products were studied by the radiochromatographic method. Interconversion of the primary and secondary alcohols was not observed. The genetic relationships between the products according to scheme (32) was studied:



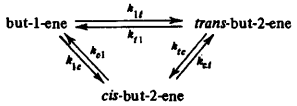
(32)

Determination of the rates in this scheme showed that most of the but-2-enes are obtained directly by the decomposition of butan-2-ol, and not by the isomerisation of but-1-ene, although the rate of isomerisation of but-1-ene into but-2-enes is also appreciable. The ratio of the rates of dehydration of butan-1-ol and the isomerisation of but-1-ene did not change on going from A-1 alumina to fluorinated alumina, indicating that the rates of dehydration and isomerisation change in the same sense on going from one alumina specimen to the other.

Butan-2-ol gave a relatively larger quantity of but-1-ene on the fluorinated alumina. The acidity of the surface apparently influences the selectivity of the dehydration of the secondary alcohols. The specific radioactivity of *trans*-but-2-ene was always greater than that of *cis*-but-2-ene, so that the *cis*- and *trans*-but-2-enes are formed by independent paths and through different intermediate surface compounds, whose interconversion is possibly difficult.

10. ISOMERISATION OF BUTENES

Hightower and coworkers [121,122], using original mixtures of two butenes, one of which was labelled with ^{14}C, showed that on catalysts based on alumina, all possible transformations of the three butenes take place according to the scheme



(33)

Thus when a mixture of *cis*-but-2-ene and but-1-ene-1-^{14}C was used, the specific radioactivity of the *trans*-but-2-ene was not greater than or equal to that of the but-1-ene in the catalysate, indicating direct formation of *trans*-but-2-ene from *cis*-but-2-ene.

It was shown that the isomerisation is a first-order reaction. By selecting rate constants to satisfy the experimental dependence of the specific radioactivities on the degree of transformation, the authors cited obtained, for example for an aluminosilicate catalyst at 23°: $k_{c_1}/k_{1c} = 0.15$, $k_{t_1}/k_{1t} = 0.04$, and $k_{tc}/k_{ct} = 0.26$.

Examination of the selectivity of the processes of butene isomerisation led the authors cited to the conclusion that the reaction takes place by different mechanisms on different catalysts based on alumina. Thus in the case of the aluminosilicate catalyst the selectivity of the isomerisation was independent of the butenes used as starting material, the origin of the catalyst and its degree of poisoning, and temperature, in agreement with the idea that a common intermediate compound is formed; this was assumed to be the classical s-butyl carbonium ion:

$$CH_3\overset{+}{C}HCH_2CH_3. \qquad (34)$$

With alumina, however, the selectivity depended to a marked extent on the butenes used as starting material, and this does not agree with the suggestion that the reaction takes place through a common intermediate compound. In this respect, fluorinated alumina is intermediate between the aluminosilicate and alumina. These results show good agreement with other observations and conclusions [119,120] regarding the isomerisation of butenes under the conditions of the dehydration of butanols on Al_2O_3.

11. DEHYDROGENATION OF HYDROCARBONS

The dehydrogenation of hydrocarbons, leading to the formation of alkenes or aromatic hydrocarbons, is an important industrial reaction. In the study of this process, Balandin and coworkers were the first to use the kinetic isotopic method under the conditions of heterogeneous catalysis. The studies were carried out in a flow assembly on a chromium catalyst (KI) with dilution by water vapour [123-127] and on an aluminium–chromium catalyst (K-544) at reduced pressure [127,128].

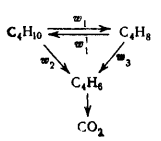
Mixtures of butane and butene in which one of the components contained ^{14}C were studied. The dependence of the experimentally determined specific radioactivities and the concentrations of butane, butene, butadiene, and carbon dioxide (or the carbonaceous deposits on the catalyst) on the duration of contact were examined. Experiments were also carried out on the dehydrogenation of mixtures of butane and butene with added labelled butadiene [125].

The chief source of loss in the dehydrogenation of butane and butene is by deposition of carbon, or, when the process is carried out with dilution by water vapour, by the formation of carbon dioxide.

The specific radioactivity of the carbon dioxide in all instances was found to be very close that of the butadiene obtained, and calculation of the rates of decomposition of butane, butene, and butadiene to carbon dioxide showed that these rates are in the ratio 1 : 4 : 60. Thus more than 90% of the carbon dioxide is obtained from the butadiene formed [125]. These results show qualitative agreement with the results of an earlier study [128], in which it was found that in the dehydrogenation of butane with the addition of labelled butene over a chromium catalyst the extent to which butane takes part in the formation of the carbonaceous deposits amounted to only 25%.

The results obtained show that the formation of carbon dioxide in the experiments with water vapour and the formation of carbonaceous deposits in the experiments in a vacuum are related processes, and led to the suggestion that water vapour in the dehydrogenation prevents the formation of carbonaceous deposits on the catalyst by oxidising the corresponding intermediate products [125].

With the assumption that the overall process can be represented by the scheme:



(35)

the value of the specific radioactivity of the butadiene was used to estimate the rate ratio $w_2 : w_3$; the values found were 1 : 1000 for the KI chromium catalyst and 1 : 25 for the aluminium–chromium catalyst. The calculations showed that for both catalysts the proportion of butadiene obtained by the consecutive path through butene is greater than 90%.

Comparison of the results shows that the ratio of the rates of the dehydrogenation of butane to butene and to butadiene is approximately the same for the two catalysts ($w_1 : w_2 \simeq 20 : 1$). The ratio of the rates w_2 and w_3 is different for these catalysts, however. Thus the formation of butadiene is a consecutive process with the intermediate formation of butene and its desorption from the catalyst surface. This result is important for the kinetics of dehydrogenation and shows that in accordance with the theory of reaction on quasi-donor surfaces, the constants of the kinetic equation in this instance have the significance of adsorption coefficients [127].

In the experiments with the chromium catalyst it was found that the rates of the transfer of the radioactive tracer from butane to butene and from butene to butane at 635° are similar [123,124,129].

Since the thermodynamic equilibrium

$$C_4H_{10} \rightleftarrows C_4H_8 + H_2 \qquad (36)$$

under the conditions of the experiments was displaced considerably to the right, it must be assumed that redistribution of the hydrogen takes place between butane and butene:

$$\begin{array}{l} CH_3{-}CH_2{-}CH_2{-}CH_3 \\ {}^{14}CH_3{-}CH_2{-}CH{=}CH_2 \end{array} \rightarrow \begin{array}{l} CH_3{-}CH_2{-}CH{=}CH_2 \\ {}^{14}CH_3{-}CH_2{-}CH_2{-}CH_3 \end{array} \qquad (37)$$

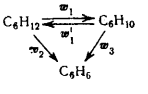
Since the products of this reaction do not differ from the starting materials (if we do not consider the isotopic composition), the equilibrium constant at any temperature should be close to unity, so that the rate constants in the forward and back directions should be approximately equal.

A number of interesting observations are reported in papers by Roginskii and Yanovskii and coworkers, who used radiochromatography to study the transformations of mixtures of butenes containing a radioactive tracer over dehydrogenating [130,131] and bismuth–molybdenum [132] catalysts. In particular, it was shown that the dehydrogenation is accompanied by cis–trans isomerisation of the butenes.

Radiochromatography and Neiman's method have been used in Balandin's laboratory to study the mechanism of the dehydrogenation of cyclohexane and methylcyclohexane over a number of catalysts.

In the multiplet theory, doublet and sextet models of the dehydrogenation of cyclohexane on oxide and metallic catalysts respectively have been developed [133]. In later papers, the sextet mechanism has been introduced for the interpretation of data obtained on oxide catalysts [134,135]; on the other hand, a number of authors [136–139] relate the hydrogenation–dehydrogenation of cyclohexane on metallic catalysts to the intermediate formation of cyclo-alkenes. Conclusions regarding the relationship between cyclo-alkenes and the process of benzene formation are based on indirect results.

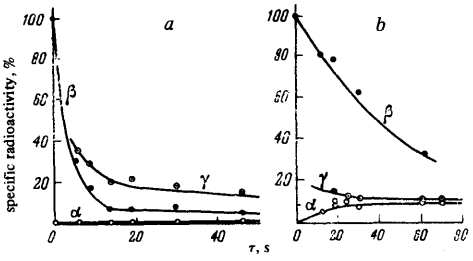
For the dehydrogenation of cyclohexane with the addition of labelled cyclohexene, studies have been made [140,141] of genetic relationships according to the scheme:



(38)

over metallic rhenium [140] and chromium oxide [140] and holmium oxide [141] catalysts; the rates of the analogous transformations of methylcyclohexane with the addition of labelled methylcyclohexene over a chromium catalyst have been determined [142].

The Figure illustrates two examples of the determination of the specific radioactivities of the products in catalysates for chromium and rhenium catalysts. It can be used to obtain information on the reaction mechanism in qualitative form by means of relationships (19) and (20).



Dependence of the specific radioactivities on the duration of contact: a: chromium catalyst; α-methylcyclohexane, β)-methylcyclohexene, γ-toluene; b: rhenium catalyst; α-cyclohexane, β-cyclohexene, γ-benzene.

For the chromium catalyst, the curve for the specific radioactivity of toluene lies above the curve for methylcyclohexene. This indicates a consecutive path with the intermediate formation of the cyclo-alkene. On the other hand, for the rhenium catalyst the specific radioactivity of cyclohexene is much greater than that of benzene ($\beta > \gamma$), indicating the direct formation of the aromatic hydrocarbon without the intermediate formation of the cyclo-alkene. Calculation of the rates of scheme (38) from Eqns. (13)–(16) confirms these conclusions, but shows that the direct formation of benzene or toluene also takes place on chromium oxide in addition to the consecutive reactions. The calculation of the rates also shows that the chief path by which cyclohexene is transformed is by dehydrogenation to benzene on the chromium catalyst and by hydrogenation to cyclohexane on the rhenium catalyst. On holmium oxide at 560° the ratio of the rates of scheme (38) is the same as that for chromium oxide.

In the doublet mechanism there should be a consecutive path for the dehydrogenation. Thus the experimental confirmation of the consecutive path for the formation of benzene (and also toluene) on chromium oxide and on holmium oxide, in contrast to the results for the rhenium catalyst, indicate than on these catalysts the dehydrogenation may take place by a doublet mechanism.

The results indicate a similarity in the mechanisms of dehydrogenation on oxide catalysts, which differ significantly from the mechanism of formation of benzene on metallic rhenium catalyst.

Tétényi and coworkers [143] suggest that over a metallic nickel catalyst the dehydrogenation of cyclohexane takes place by a consecutive path, since in experiments with

mixtures of labelled cyclohexane and non-labelled cyclohexene they detected transfer of the tracer to the cyclohexene. In this work, however, the specific radioactivities of the products were not determined, so that there is insufficient justification for this conclusion. It is possible that the cyclohexene was obtained under the conditions of the experiments by a parallel-consecutive scheme.

12. DEHYDROCYCLISATION OF PARAFFINIC HYDROCARBONS

A recently published review[144] on the dehydrocyclisation of paraffinic hydrocarbons examined the most important work in this field, including work carried out by the labelled atom method with ^{14}C. Work carried out by the labelled molecule method appeared only recently and was not included in the review[144].

The problems of the mechanism of dehydrocyclisation which can be solved by this method relate chiefly to the possibility of establishing stepwise mechanisms involving the participation of unsaturated compounds with an open chain or cyclic six-membered compounds as intermediate products.

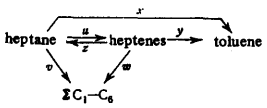
Table 1. Dehydrocyclisation of hydrocarbons on a potassium–aluminium–chromium catalyst[145].

Original mixture	Volume rate, h^{-1}	Specific radioactivity, counts min^{-1} (mg $BaCO_3$)$^{-1}$		
		heptane	heptene	toluene
n-Heptane + hept-1-ene-4-^{14}C	2.1	34	258	254
	7.4	32	280	226
n-Heptane-4-^{14}C + hept-1-ene	2.1	253	75	82
	7.5	288	58	66
n-Heptane + hept-2,3-enes-4-^{14}C	2.2	28	250	258
	7.2	34	291	274

Results obtained by Lipovich and coworkers[145] on the dehydrocyclisation of paraffinic hydrocarbons on an aluminium–chromium–potassium catalyst indicate that this reaction takes place with the intermediate formation of the alkene. Table 1 gives the characteristic values of the specific radioactivities of the chief products, obtained in experiments with mixtures of alkanes and alkenes.

Despite the slight scatter in the results, it can be seen from Table 1 that the specific radioactivities of toluene are extremely close to those of the alkenes, indicating a consecutive path for the reaction. The slight decrease in the value of the specific radioactivity of toluene compared with the values for alkenes at high volume rates is apparently due to the fact that under these conditions, adsorption equilibrium is not established between the alkene in the gaseous phase and on the catalyst surface.

From the results obtained, Lipovich and coworkers[36] calculated the "intensities" of the processes in the scheme:



(39)

The authors cited found the value of y by multiplying the mole fraction of the heptane taken by the fraction of the radioactivity converted into toluene; the value of x was found as the difference between the quantity of toluene formed and y, etc. As expected, the alkene is converted into toluene more rapidly than the alkane (that is $y \gg x$)†.

The authors cited also found that in mixtures with heptane, labelled hept-2,3-ene was converted into toluene much more slowly than hept-1-ene; this was attributed to the more intensive deposition of carbon on the catalyst by hept-2,3-ene, leading to a decrease in its activity. It may be suggested, however, that in this instance an important part is played by the specific orientation of the molecule on the catalyst surface as a result of the interaction of the π electrons of the double bond with the surface.

A study of the same reaction on metallic Ni, Pt, and mixed (Ni/Al_2O_3, Pt/Al_2O_3) catalysts was described by Tétényi and Paal[146,147]. Using a pulse procedure and radiochromatography, the authors cited reached analogous conclusions regarding the consecutive nature of the reaction, and showed that in the dehydrocyclisation of hexane, alkenes and dialkenes with the normal structure are intermediate products, whereas cyclanes and cyclenes are not formed. Characteristic values of the specific radioactivities of the products in arbitrary units from various series of experiments are given in Table 2.

Table 2. Dehydrocyclisation of hydrocarbons on metallic catalysts.

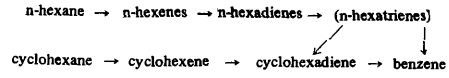
Catalyst	Original mixture	Specific radioactivities of products (arbitrary units)					Refs.
		n-hexene	n-hexane	cyclohexane	cyclohexene	benzene	
Pt	n-Hexane-1-^{14}C	0.5	33.5	—	—	34	146
Ni/Al_2O_3	n-Hex-1-ene, n-Hexane-1-^{14}C	36.5	4.8	—	—	4.6	146
Pt	n-Hex-1-ene, n-Hexane-1-^{14}C, cyclohexane	64	80	1.6	—	27	147
Pt	n-Hexane, cyclohexane-^{14}C	background level	—	38	—	15	147
Ni/Al_2O_3	n-Hexane-1-^{14}C, cyclohexane	52*	—	0.9	—	10	147
Pt	n-Hex-1-ene-1-^{14}C, cyclohexane	94	94	0.5	22**	63	147
Pt	n-Hex-1-ene-1-^{14}C, cyclohexene	74*	—	—	6	52	147
Pt	Hex-1-ene-1-^{14}C, cyclohexa-1,3-diene	355*			6.3***	2.6	147

*Hexane + hexenes.
**Cyclohexane + hexadienes.
***Cyclohexa-1,3-diene.

By comparing their own and published results on the mechanism of the dehydrocyclisation of alkanes, the authors cited concluded that the main features of the mechanism of this reaction are the same for metallic and for oxide catalysts, and that for hydrocarbons with an open chain and for

† In the interpretation of the results obtained it is important to remember the inadequacy of the concepts of intensity and reaction path. For example, the observed magnitude of the intensity x by itself does not make it possible to conclude that heptane under the conditions of the experiments is converted directly into toluene: the intensity x merely shows that part of the heptane is converted into toluene by some means or other (possibly through the alkene).

cyclic hydrocarbons the mechanism can be described by the scheme:



(40)

Experiments with mixtures of labelled hex-1-ene and hexatriene showed[148] that the latter is in fact an intermediate product in the formation of cyclohexadiene and benzene on a platinum catalyst. The relatively low value of the specific radioactivity of hexatriene compared with that of cyclohexadiene and benzene in the catalysates, however, may indicate that there is another reaction path by which the dialkene undergoes cyclisation.

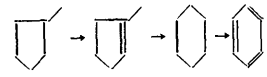
13. HYDRO-DEHYDROISOMERISATION OF CYCLANES

A number of papers describe the use of radiocarbon to study the mechanism of the interconversion of methylcyclopentane, cyclohexane, and benzene in an atmosphere of hydrogen over bifunctional (oxide–metallic) catalysts, and also over tungsten sulphide. Kalechits and coworkers[149,150] showed that when cyclohexane is heated with labelled benzene in an autoclave over tungsten sulphide, the product is methylcyclopentane, whose specific radioactivity is greater than that of the cyclohexane in the catalysate.

When a mixture of benzene and labelled cyclohexane was used, the specific radioactivity of the latter in the catalysate was greater than that of the methylcyclopentane; radioactivity was not detected in the benzene. When mixtures of cyclohexane and methylcyclopentane were passed over a platforming catalyst[151], the radioactivity of the cyclohexane in the catalysate was considerably greater than that of the benzene when the cyclohexane was labelled; when the methylcyclopentane was labelled, however, the specific radioactivities of the cyclohexane and benzene in the catalysate were approximately equal. According to conditions (19) and (20), these results show that on both catalysts studied, the interconversion of methylcyclopentane and benzene takes place partly without desorption of any intermediate substances, including cyclohexane; the other reaction path lies through cyclohexane. It has been shown[152] that the concentration of non-stoichiometric sulphur has no influence on the overall rate of hydrogenation of benzene, but influences the ratio of the rates of the two paths for the formation of methylcyclopentane. The authors cited believe that on the surface of the catalyst the cyclic hydrocarbons undergo a number of transformations, including the intermediate formation and isomerisation of cycloalkenes, which may not be related to the gaseous phase by an adsorption equilibrium. These ideas formed the basis of the familiar stepwise scheme for the reforming of cyclanes, proposed by Mills and coworkers[153].

The experimental justification for this scheme was provided by the characteristic properties of bifunctional catalysts combining the dehydrogenating properties of metals of the platinum group with the isomerising properties of an acidic oxide. The theoretical justification was the possibility of applying the ideas of the mechanism of homogeneous isomerisation in accordance with Whitmore's concept, with the formation of a carbonium ion as a result of the reaction of a proton of the catalyst with the π electrons of the double bond of the alkene. An analysis of published results shows that although this scheme has been in existence and has been used for 15 years, there are no results which confirm it directly or indicate the part played by cyclenes as intermediate products, in particular in the isomerisation and dehydrogenation of cyclohexane and the dehydroisomerisation of methylcylopentane.

To obtain these results, experiments were carried out[154–159] with cyclohexane and methylcyclopentene. Studies were made of the transformation of methylcyclopentane into benzene according to the scheme[157]:



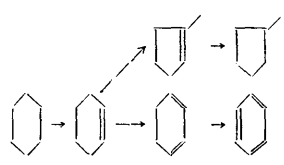
(41)

The experiments were carried out in a flow assembly at a pressure of 20 atm and 480°, at a molar ratio of hydrogen to carbon equal to 5 : 1, on a number of specimens of bifunctional catalysts (platinum on alumina and palladium on alumina). The reaction products were analysed by radiochromatography. Labelled methylcyclopentene was added to the original methylcyclopentane. In accordance with Eqns. (19) and (20), if the methylcyclopentene were a necessary intermediate product [according to scheme (41)], its specific radioactivity into the catalysate should be less than that of benzene or cyclohexane.

A detailed study of the reaction products indicated that dehydroisomerisation of the five-membered rings, splitting of the rings, and hydro-cracking with the formation of lower molecular-weight products take place. It was found that the specific radioactivity of benzene and cyclohexane were close to that of methylcyclopentane and much less than that of methylcyclopentene, and this contradicts the above scheme. A remarkable feature was that the specific radioactivities of the lighter hydrocarbons, particularly the pentanes, was very high and in a number of instances exceeded the specific radioactivity of the methylcyclopentene. This means that methylcyclopentene is an intermediate product in the hydro-cracking. The marked difference in the specific radioactivities of the products of the cracking and the products of the isomerisation of the cyclo-alkanes indicates that these processes take place through different intermediate surface compounds. The similarity in the specific radioactivities of the methylcyclopentane, cyclohexane, and benzene apparently indicates not only that methylcyclopentene is not a necessary intermediate product, but also that methylcyclopentane undergoes isomerisation more rapidly than methycyclopentene.

Similar results were obtained[160] when methylcyclopentane and labelled methylcyclopentene were passed over AP-56 catalyst under the conditions of platforming. The authors cited point out that if methylcyclopentane forms a complex "corresponding to the cyclo-alkene structure", it differs from the complex obtained directly from the unsaturated hydrocarbon.

The transformation of cyclohexane and cyclohexene according to scheme (42) was studied on catalysts consisting of palladium on alumina, rhenium on alumina, and molybdenum oxide on alumina[155].



(42)

A mixture of labelled cyclohexane and cyclohexene was used. In this instance, if the cyclohexene were an intermediate product, its specific radioactivity in the catalysate should have been greater than that of the benzene

and methylcyclopentane. Radiochromatographic analyses showed the opposite, however. Radioactivity was detected in methylcyclopentane and benzene, but not in cyclohexene. This indicates the possibility of isomerisation of cyclohexane independently of cyclohexene; the latter is not an intermediate product. Later, a similar result was obtained[160] when a mixture of cyclohexane and labelled cyclohexene was passed over an AP-56 platinum catalyst under the conditions of platforming.

It is now assumed by a number of authors[161-163] that in reforming reactions the intermediate alkenes are not only formed, but are necessarily desorbed. In early papers, however, it was suggested that the alkene may undergo further transformation without desorption. In some studies[154], cyclohexene remained in the catalysates, so that it was either desorbed or did not reach the catalyst surface during the reaction.

Special experiments with deuterium[155] showed that at atmospheric pressure the cyclohexene of the original mixture takes part in deuterium exchange almost quantitatively, so that it passed through a stage involving adsorption on the catalyst.‡ In experiments under pressure, the degree of exchange was also fairly high, and some of the molecules of the cyclohexene remaining had undergone multiple exchange. Almost no exchange took place in the absence of a catalyst.

These results showed that the transformations of the cyclo-alkanes and -alkenes under the conditions studied apparently take place by independent paths. In this connection, the problem of the mechanism of the action of bifunctional reforming catalysts is becoming more urgent.

The solution of this problem will make it possible to improve the technology of one of the most important petrochemical processes.

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The material examined shows that the LM method is most effectively used in the study of the mechanism of multi-stage catalytic reactions, when the usual chemical methods lead to ambiguous results and it is necessary to make a choice between several possible reaction paths. This situation usually arises at a definite stage in the experimental study of a given process. Thus the reactions studied are often familiar reactions for which definite views, widely encountered in scientific circles, already exist regarding the mechanism. The use of the LM method makes it possible in many instances to develop significantly more penetrating views regarding the mechanisms of these processes; in some instances the results are extremely unexpected and make necessary a new approach to the interpretation of familiar results and stimulate their further study at a new and higher level.

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Zelinskii Institute of Organic Chemistry,
Academy of Sciences of the USSR,
Moscow

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Mechanism of the Catalytic Hydrogenation of Oxides of Carbon to Methane

V.M.Vlasenko and G.E.Yuzefovich

The present review examines the mechanisms of the formation of methane from carbon monoxide and dioxide and hydrogen in the presence of contact catalysts based on metals of the iron group (chiefly nickel). The experimental results obtained by various methods are examined, the reactive forms of the adsorbed molecules and the signs of their charges are considered, and particular attention is paid to the determination of the reactive complexes under the conditions preceding the start of the catalytic reaction, and the results of kinetic studies. It is shown that there is a significant difference in the mechanisms of the hydrogenation of carbon monoxide and dioxide to methane. This difference is attributed to the poisoning effect of carbon monoxide on the processes involved in the hydrogenation of CO_2. Attention is drawn to a number of results which are of considerable importance for the solution of the problems of the catalytic purification of hydrogen from oxides of carbon. The bibliography contains 129 references.

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I. INTRODUCTION

Syntheses based on carbon monoxide and hydrogen (and to a much smaller extent on carbon dioxide and hydrogen), from their discovery[1-3] up to the present, have attracted considerable attention from many research workers. This is due to the variety of possibilities for the practical utilisation of reactions involving the catalytic hydrogenation of oxides of carbon. A large number of versions of the synthesis of hydrocarbons, the synthesis of methanol, and the direct synthesis of higher alcohols[4,5] are among the reactions of carbon monoxide with hydrogen which have been carried out on the industrial scale.

The possibilities of synthesis from oxides of carbon and hydrogen apparently have not been fully realised. Moreover, with other components in the reaction mixture it is possible to carry out the most rational production of complex end products. Examples of such processes are the preparation of higher alcohols by the oxo-process[5] and the synthesis of amines from carbon monoxide, hydrogen, and ammonia[6,7].

The mechanisms of all these reactions and of other reactions which have not yet been realised but which are thermodynamically possible may be the same in the initial stages, so that the study of these stages is of considerable interest. Usually, however, the compositions of the reaction products are complex, and this makes it very difficult to obtain a true picture of the process. If, however, we exclude from consideration some stages of the reaction, it is possible to simplify the problem and to concentrate attention on the study of the first stages of the synthesis. This can be done by studying the formation of methane, since in this way it is possible to investigate in purest form the primary stages of the reaction of oxides of carbon with hydrogen. This possibility has been underestimated, apparently because there are no reviews devoted specially to the mechanism of the synthesis of methane, whereas studies of the mechanism of formation of the higher hydrocarbons are published periodically[8-16].

As the simplest aliphatic hydrocarbon, methane exhibits the basic features of its homologous series, so that the study of the mechanism of its formation is of primary importance in the investigation of the synthesis of alkanes.

In this study, it is naturally necessary to choose reaction conditions under which the formation of methane is the only process or at least the predominant process. A decisive feature is the selection of a highly selective and active catalyst, in the presence of which the most definite results are obtained; it is also desirable that the results be of practical use.

Nickel is one of the most active catalysts for the synthesis of methane from carbon monoxide and hydrogen[17]. The other metals of the iron group have lower activities. Nickel, cobalt, and iron can be arranged in the same sequence with reference to the conversion of carbon dioxide into methane[1,2,18-22]. The present review deals chiefly with results obtained with nickel catalysts, which in our view are of greatest interest.

II. MECHANISM OF THE FORMATION OF METHANE FROM CARBON MONOXIDE AND HYDROGEN

The hydrogenation of carbon monoxide to methane can be regarded as the simplest example of the synthesis of hydrocarbons. This makes it possible on the one hand to introduce existing theories of the synthesis of hydrocarbons to explain the mechanism of formation of methane, and on the other hand, as shown above, it makes it possible to some extent to use the results obtained to understand the mechanism of formation of higher hydrocarbons.

The earliest theory of hydrocarbon synthesis was the carbide theory[23-27], which was subsequently found to be inadequate to explain these processes in the presence of catalysts based on metals of the iron group[9]. In fact, carbide formation cannot be an intermediate stage in the synthesis of methane from carbon monoxide and hydrogen, since the temperature of hydrogenation of the surface nickel carbide is higher than the temperature of appreciable methane formation[28] and the rate of the synthesis is much greater than the rate of carbide formation[29-33].

Other widely held ideas, in addition to the carbide theory, have included various schemes according to which oxygen-containing substances—methanol[34] or formaldehyde[5]—are intermediate products. Attempts to detect formaldehyde or methanol in the synthesis of methane on a nickel catalyst were unsuccessful, however[35]. Moreover, it was shown[36] that on a cobalt catalyst the yield of hydrocarbons when methanol is used as starting material is less than that obtained when a mixture of carbon monoxide and hydrogen is used. The formation of hydrocarbons from methanol is evidently a secondary process involving carbon monoxide and hydrogen obtained by the decomposition of methanol.

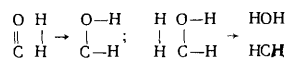
A suggestion related to these hypotheses was put forward by Fischer and coworkers[17], according to whom the reaction with carbon monoxide leads to the intermediate formation of the metal carbonyl, which is then reduced with the formation of methane. A similar explanation for the synthesis of hydrocarbons was put forward by Pichler[5,16].

In contrast to early hypotheses based on Sabatier's theory of phase intermediate compounds[37], the idea of primary compound formation represents a definite change towards modern theories of catalytic action, which make use of the concept of intermediate *surface* compounds[38,39]. In connection with these theories, the search for reactive surface complexes and radicals is acquiring primary importance.

Orlov's suggestion[40] that methylene radicals are formed in the primary stages of the hydrogenation of carbon monoxide

$$CO + 2H_2 \rightarrow CH_2 + H_2O$$

was later verified experimentally by Eidus and Zelinskii[41], who proved the existence of CH_2 radicals in the methylation of benzene to toluene. It was established that the CH_2 species are formed from carbon monoxide and hydrogen[29]. On the basis of the results obtained, Eidus[36] concluded that on cobalt and nickel contact catalysts the primary stages of the process involve the successive hydrogenation of carbon monoxide first to an unstable oxygen-containing group, and then to the methylene radical:



A similar mechanism was proposed by Hamai[42].

The idea that an adsorbed complex of HCOH is formed provided the basis of the mechanism of hydrocarbon synthesis proposed by Anderson[5,43]. This mechanism differs from Eidus' scheme[9] in the subsequent stages of hydrocarbon chain formation. In a study of syntheses based on carbon monoxide and hydrogen in the presence of iron catalysts, Bashkirov and coworkers[44-46] also concluded that these processes should involve the production of an unstable intermediate adsorption complex which contains carbon, hydrogen, and oxygen atoms and is the precursor of both hydrocarbons and alcohols.

The conclusion that an intermediate compound of this kind exists was also reached[47] on the basis of a study of the Fischer–Tropsch synthesis in the presence of a nickel catalyst. Similar ideas were put forward by Eidus[48] and by Gibson and Clarke[49] on the basis of a study of the synthesis of hydrocarbons from carbon monoxide, hydrogen, and ethylene.

Thus irrespective of the composition of the products, the formation of a primary complex is assumed in all schemes of catalytic synthesis from carbon monoxide and hydrogen. The existence of this compound has not yet been confirmed experimentally, however, although this problem is a central problem in the study of the mechanisms of various reactions of carbon monoxide with hydrogen.

The possibility of existence of *adsorption complexes* in itself does not prove that they play a leading part in the reactions. In order to reach this conclusion it is necessary to rely on the results of direct kinetic studies, which make it possible to determine the limiting stage of the reaction.

The available data[50,51] indicate that the adsorption of the components of the reaction cannot be taken as the limiting stage. Similarly, the desorption of the reaction products does not determine rates of hydrogenation on nickel contact catalysts[50]. Study of the infrared spectra of water[52] showed that it is not adsorbed on a nickel contact catalyst, and it has also been shown[53] that methane and water are not adsorbed on a nickel–chromium catalyst.

On the other hand, the results of kinetic studies of the process indicate that the rate of formation of methane is determined by the reaction of carbon monoxide and hydrogen adsorbed on the surface of the contact catalyst.

It has been found by the static method[54] that at 271° and H_2/CO ratios from 2 to 20 in the presence of a nickel wire catalyst the rate of formation of methane is approximately proportional to the pressure of hydrogen and is retarded by carbon monoxide. A similar conclusion was reached by Luyten and Jungers[55], who studied the formation of methane in a static system at 300° and H_2/CO ratios from 1 to 6 in the presence of nickel deposited on kieselguhr. The reaction rate was given by the equation

$$W = k \cdot p_{H_2}^{0.9} \cdot p_{CO}^{-0.2}.$$

The heat of activation was 27 kcal mole^{-1}. This value differs considerably from the value 35 ± 1 kcal mole^{-1} found by Nicolai and coworkers[56], although the studies were carried out under identical conditions, on similar contact catalysts. The discrepancy is apparently due to the non-steady state of the catalyst surface.

The flow method has been used[50] to make a detailed study of the kinetics of the synthesis of methane at atmospheric pressure on an industrial nickel–kieselguhr contact catalyst in the range 300–350° at H_2/CO ratios from 1.2 to 4. The limiting stage of the process is the reaction between a molecule of carbon monoxide adsorbed on the contact surface and three molecules of hydrogen, according to the equation

$$W = \frac{p_{CO} \cdot p_{H_2}^3}{(A + Bp_{CO})}$$

where A and B are constants.

The retarding influence of carbon monoxide at high concentrations, observed in the works cited, is apparently due to the fact that the CO covers the contact surface to a considerable extent, leading to a corresponding decrease in the degree of covering of the surface by hydrogen. Moreover, in this instance there is a possibility of a change in the phase composition of the contact catalyst as a result of the formation of nickel carbides. Changes in the phase composition can be avoided if the studies are carried out at low concentrations of carbon monoxide in a large excess of hydrogen. The kinetic relationship obtained in this way by a flow-circulation method with a nickel–chromium catalyst at 135–175° and a concentration of carbon monoxide in hydrogen equal to 0.3 vol. % has the form[57,58]

$$W = k \cdot p_{CO}^0 \cdot p_{H_2}^0$$

which indicates directly that the process takes place by a Langmuir–Hinshelwood mechanism. The zero order of

the reaction with respect to both components can be attributed to the non-uniformity of the nickel surface with respect to the adsorption of carbon monoxide and hydrogen under the given conditions. Non-uniformity of the surface with respect to the adsorption of hydrogen at room temperature was established[59-61] by the differential isotopic method, and the non-uniformity of the surface of iron catalysts in the synthesis of hydrocarbons has also been observed[62]. Studies by a method enabling the change in the weight of the catalyst during the contact process[57] to be observed established that under the conditions of the experiment at 160° the degree of covering of the nickel surface by carbon monoxide amounts to about 1/3, and 2/3 of the surface is covered with hydrogen. This apparently explains the fact that the heat of activation (16.2 kcal mole^{-1}) is less than that in the works cited above[55,56], in which the degree of covering of the surface by carbon monoxide might have been much greater, because of the high concentration of CO in the gaseous phase. From these results it follows that in all examples of the synthesis of methane and higher hydrocarbons from carbon monoxide and hydrogen, on nickel catalysts at least, the reaction components interact in the adsorbed layer. This indicates that the adsorption complexes produced may play a leading role in syntheses from carbon monoxide and hydrogen. The detection of these complexes is therefore of considerable interest in the investigation of the mechanism of the catalytic formation of hydrocarbons.

The formation of adsorption complexes can be established if their steady-state concentration is sufficiently high. To determine the temperature range corresponding to the existence of adsorption complexes, it is necessary not only to establish that the limiting stage is the reaction in the adsorption layer, but also to establish whether the rate of the catalytic reaction is controlled by the rate of formation or the rate of transformation of the complexes. These stages can be studied experimentally by measuring the temperature dependence of the contact potential difference (c.p.d.) in the reaction mixture. The formation of adsorption complexes generally leads to a marked change in the contact potential difference relative to the values for each of the reagents.

For example, in the reaction of carbon monoxide and hydrogen on zinc oxide a decrease in the value of the c.p.d., which remained constant at the temperatures of catalysis, was observed[63]. In this instance the rate of the hydrogenation of carbon monoxide is limited by the rate of transformation of the adsorption complexes formed[64]. A different picture is observed in the hydrogenation of carbon monoxide in the presence of a nickel–chromium contact catalyst[65]. The temperature dependence of the c.p.d. is given by a characteristic curve with a minimum corresponding to the highest concentration of the adsorption complexes. With increase in temperature the value of the c.p.d. under the conditions of catalysis becomes close to its value for the adsorption of carbon monoxide. This indicates that the catalyst surface carries adsorbed carbon monoxide, and the rate of the contact process is determined by the rate of its conversion into chemisorption complexes. Thus in the reduction of carbon monoxide to methane on nickel, the rate of formation of the reaction complexes is the rate-determining stage of the reaction. It may be assumed that this is also true of the synthesis of methane from carbon monoxide and hydrogen in the presence of catalysts based on iron and cobalt.

It is clear from the foregoing that studies carried out under the conditions directly preceding catalysis are of greatest value in the investigation of the mechanism of the process. The study of the adsorption of the reaction components under these conditions, both separately and in mixtures, is acquiring primary importance, and may give important information on the formation and composition of the adsorption complexes.

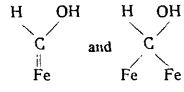
In spite of an extensive literature devoted to the adsorption of hydrogen and carbon monoxide on metallic contact catalysts, however, comparatively few studies have been made of the adsorption of these reagents and their mixtures under conditions close to those of catalysis or at the temperatures of catalysis.

Among studies of this kind carried out for cobalt Fischer–Tropsch contact catalysts, mention may be made of studies[66-71] of the adsorption of carbon monoxide and hydrogen, and their mixtures, in the range 25–97°. It was shown that at 97° over a period of 12 h, the formation of hydrocarbons, water, or carbon dioxide from CO and H_2 is not observed, whereas at 110°, methane was detected in the gas[67]. Special experiments established that cobalt carbonyls are not formed at 53, 76, or 97°,[70] that is the adsorption relationships were studied on an almost unaltered contact surface. In the study of the adsorption of mixtures of CO and H_2 it was established that the adsorption of each gas from the mixture is greater than the adsorption of the individual gas at the same partial pressures. With increase in the total pressure, the adsorption of carbon monoxide is greater from the mixture with $CO:H_2 = 1:2$ than from the mixture with $CO:H_2 = 1:1$. The adsorption of hydrogen is characterised by the opposite relationship[66,69]. With increase in temperature the quantity of adsorbed hydrogen increases, the dependence of the quantity of adsorbed carbon monoxide on the quantity of adsorbed hydrogen tending towards a linear relationship, and this, in the opinion of the authors cited[66], may indicate the formation, on the catalyst surface, of chemisorbed complexes which are possibly intermediate products in the Fischer–Tropsch synthesis. The same conclusion was reached by the other authors cited[69], who showed that the ratio of carbon monoxide and hydrogen adsorbed on the contact surface reaches 1 : 1 at 97°. This may indicate the formation of a complex with the composition HCOH. In other work[67], however, the value of this ratio for the same temperature was 2 : 1, and it was concluded that the complex ≡C–H is formed. The mutual intensification of adsorption, observed with consecutive adsorption of the components[68,70,71], also indicates strong chemical interaction between carbon monoxide and hydrogen in the adsorption layer.

These results of adsorption measurements on cobalt contact catalysts, however, cannot establish sufficiently clearly the compositions of the stoichiometric chemisorption complexes[72]. This is due, in particular, to the lack of information on the chemisorbed forms of the molecules of carbon monoxide and hydrogen and their reactivities; this makes it impossible to reach definite conclusions regarding the participation of various forms of chemisorbed molecules in the formation of the surface complexes.

To some extent these difficulties were overcome in a study[72] of the adsorption and desorption of carbon monoxide and hydrogen on a deposited iron catalyst at 50°. As with the cobalt contact catalysts, the adsorption measurements could not prove the formation of chemisorption complexes, since it was shown that, in addition to the formation of reactive forms of the molecules, irreversible adsorption of part of the gas took place, and this fraction did not take part in the formation of complexes. To eliminate the contribution from the irreversible adsorption, the authors cited used a method involving desorption with decrease in

pressure. It was established that, irrespective of the CO : H_2 ratio in the original mixture, a gas mixture with the almost constant ratio 1 : 1 is desorbed from the contact surface after 38 h. This indicates the existence of a weakly-bound chemisorbed complex, which decomposes on desorption. After determination of the composition of the chemisorption complex, we are faced with the problem of its structure and the type of bonds present. Linear and bridged bonds are formed when carbon monoxide is adsorbed on iron [73,74]. In this connection, two structures are possible for the complex HCOH:



A choice between these structures can be made on the basis of work by Blyholder and Neff [75], who used infrared spectroscopy to study the reaction of carbon monoxide and hydrogen on the surface of a deposited iron catalyst. The authors cited established that at 180°, complexes of the type

are formed, where R may be either a hydrogen atom or a hydrocarbon radical with unsaturated bonds. Although this structure differs slightly from that proposed by Eidus, it may be concluded that it is formed by the reaction of hydrogen with carbon monoxide adsorbed in linear form. An interesting feature is that at temperatures at or close to room temperature the authors cited, in agreement with Eischens [76], did not observe reaction between carbon monoxide and hydrogen. This work [75] is almost the only proof of the existence of surface complexes obtained by infrared spectroscopy; this is apparently due to the fairly high concentration of the complexes at 180°.

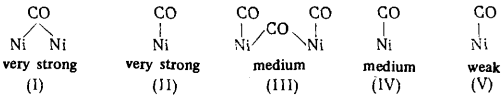
A number of studies [28,57,63,65] have been made of the reactive forms of adsorbed molecules, their interactions, and the part played by the primary complexes in the synthesis of methane from carbon monoxide and hydrogen in the presence of a nickel–chromium catalyst.

The study of the adsorption of carbon monoxide and hydrogen, separately and in a mixture, was carried out at 75°, since at low temperatures carbon monoxide may form volatile nickel carbonyls, which decompose above 60°, [77] and formation of methane begins at temperatures slightly greater than 80°. [78] Thus the conditions established corresponded to those directly preceding the start of the catalytic reaction. Under these conditions the adsorption of the gases takes place only on the nickel surface, and neither hydrogen nor carbon monoxide are adsorbed on the chromium oxide used as carrier.

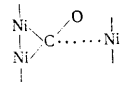
In a number of papers it has been suggested that in hydrogenation on nickel contact catalysts, hydrogen may penetrate into the interior of the catalyst, with a significant influence on the catalytic activity [79–84]. The adsorption of hydrogen and carbon monoxide was therefore studied [28,63,65] both on a clean nickel catalyst surface (treated specimens) and on specimens containing dissolved hydrogen (untreated specimens).

It was established that on the treated catalyst specimen, hydrogen is adsorbed at 75° by a dissociative mechanism, and the surface acquires a positive charge [65]. When dissolved hydrogen is present in the nickel, however, the adsorption is accompanied by the transfer of electrons from the catalyst, and the adsorbed hydrogen acquires a negative charge [65]. This result shows that dissolved hydrogen has a significant influence on the adsorption properties of nickel.

Carbon monoxide is adsorbed on nickel in molecular form. Study of the infrared spectra of the adsorbed molecules [85–87] showed the existence of at least five forms of bonding between carbon monoxide and the nickel surface, with different structures and bond strengths:



The production of a given form depends on the crystal structure of the nickel [87]. With crystalline specimens, the production of bridged (I) and linear (II) forms is observed primarily, but at higher degress of covering, linear groups are produced on nickel atoms which already have chemisorbed carbon monoxide by a bridging type of bond (III). On disordered crystallites, carbon monoxide is much less strongly chemisorbed, and only in linear structures (IV) and (V). Recently, another form of bridging bond has been found [88]:



The formation of this bond is facilitated by comparatively low pressures of carbon monoxide, when the neighbouring Ni atoms are not bonded to CO molecules by other types of bond.

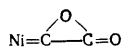
Some authors doubt the existence of bridging bonds. Thus calculation by the MO method [89] showed that all available data on the infrared spectra of chemisorbed CO can be explained by assuming only a linear form of bonding for carbon monoxide adsorbed on various surface centres. The strengths of the bonding and the frequencies of the CO stretching vibration also differ. This view is held by other authors [90], who however do not exclude completely the possibility that a small proportion of the carbon monoxide molecules are adsorbed in bridged form. These views, however, are not fully justified.

The production of the various forms of adsorbed carbon monoxide apparently depends on the conditions of the experiment. For the adsorption of carbon monoxide on a treated specimen of nickel–chromium catalyst at 75°, it was established that at low pressures the chemisorption is accompanied by the production of a bridged form of bond [type (I)], and that with increase in pressure the nature of the bonding changes, and a surface layer of the single-centre type is formed [28], in agreement with the results of other studies [85,89,91]. The layer of chemisorbed gas is positively charged, and when the bridged structure changes to the linear structure there is no change in the electronic properties of the catalyst surface [65].

Each type of adsorption should evidently be characterised by bonds of different strength between the adsorbate and the contact surface, so that the form of bonding should determine, in particular, the thermal stability of the adsorbed carbon monoxide and its stability towards hydrogenation. For the bridged structure, decomposition of carbon monoxide is not observed up to 300°, and its hydrogenation begins only above 140°. Carbon monoxide joined to nickel by a linear bond is hydrogenated at a temperature slightly greater than 80°. Thus the linear form of bonding for the adsorbed carbon monoxide is weaker than the bridging form, and hence more reactive. This form is apparently of types (IV) or (V).

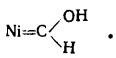
The presence of adsorbed and dissolved hydrogen in the contact catalyst influences the properties of the nickel towards the adsorption of carbon monoxide. The dissolved hydrogen alters the electronic properties of the metal. Thus changes have been observed[92] in the infrared spectra of carbon monoxide adsorbed on nickel, corresponding to the change from linear structures to bridging structures, depending on the thoroughness with which hydrogen was removed from the metal after reduction. In agreement with these observations, according to published data[28], in the adsorption of carbon monoxide on an untreated nickel–chromium catalyst, sorbed hydrogen is displaced from the contact catalyst into the gaseous phase, and a linear form of bond is produced between the adsorbed carbon monoxide and the contact surface. As with the adsorption of CO on a clean nickel surface, the layer of carbon monoxide is positively charged[65].

The influence of dissolved hydrogen on the adsorption properties of the contact catalyst is due to the two-layer adsorption of carbon monoxide[28]

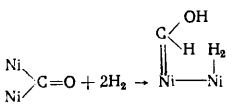


As a result of the formation of the chemisorption bond between the carbon monoxide molecule and the contact surface, the bonds in the CO molecule are weakened to such an extent that two CO molecules interact with the rupture of one carbon–oxygen bond and the formation of a carbon–carbon bond.

The determination of the forms of the adsorbed molecules makes it possible to examine the mechanism of the adsorption of carbon monoxide and hydrogen from their mixtures. Carbon monoxide is adsorbed in linear form. At the same time the adsorption of hydrogen increases. The absorption of hydrogen in the presence of carbon monoxide takes place slowly, evidently due to chemical reaction with the formation of complexes of a type corresponding to the enol form of formaldehyde:

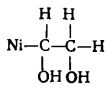


The formation of complexes of this kind also takes place if hydrogen is adsorbed on a contact catalyst on which carbon monoxide has previously been adsorbed by the two-centre mechanism. The bridged type of bond is converted into the linear type with the formation of a complex, and the molecular hydrogen is adsorbed on the liberated centres of the nickel



The mean rate of formation of the complex at 75° corresponds to the transformation of 5.6×10^{-7} cm³ CO cm^{-2} Ni h^{-1}; the concentration of adsorption complexes formed amounts to ~ 10^{15} per 1 cm² nickel surface.

The reaction between hydrogen and carbon monoxide adsorbed in two layers leads to the formation of complexes of the type



at a mean rate corresponding to the transformation of 12.8×10^{-7} cm³ CO cm^{-2} Ni h^{-1} and the concentration of the complexes amounts to ~ 3.8×10^{16} per 1 cm² nickel. The possibility of formation of carbon–carbon bonds during the adsorption of carbon monoxide and hydrogen from their mixtures was proposed[75] on the basis of a study of the infrared spectra.

The concentrations of the complexes formed are sufficient for their detection by infrared spectroscopy. This in turn would have been significant evidence for the existence of surface compounds of this type. The failure of Blyholder and Neff[52] to detect adsorption complexes on a nickel contact catalyst at 180° and above by this method can apparently be attributed to the excessively high temperature of the experiment, at which the complexes formed are readily transformed into the final products. The suggestion, made by the authors cited[52], that the reacting substances are much less firmly bound to the nickel than to the iron catalyst, on which it was possible to detect surface compounds at 180°, [75] can be disputed: at this temperature, the reaction on iron does not take place very intensively, whereas in the presence of the more active nickel the reaction rate is quite high, and this leads to a sharp decrease in the concentration of chemisorption complexes.

Unlike Koelbel and coworkers[72], Vlasenko and coworkers[28] detected stoichiometric chemisorption complexes, indicating that all the adsorbed carbon monoxide has the same reactivity.

Thus surface compounds of at least two types—a type corresponding to the enol form of formadehyde and a type containing two carbon atoms—may be formed on the surface of the nickel contact catalyst, depending on the conditions of adsorption. The existence of complexes with two carbon atoms indicates that under certain conditions of the synthesis of hydrocarbons, at least on nickel contact catalysts, carbon–carbon bonds may be produced even in the stage of carbon monoxide adsorption. The possibility of existence of primary complexes not only with one carbon atom but also with a larger number of carbon atoms was pointed out by Eidus[10]. The possible role of complexes of this type in the synthesis of hydrocarbons requires further detailed study, but they are not formed in the hydrogenation of carbon monoxide in a large excess of hydrogen, since only methane and water are detected in the reaction products.

The information obtained in the study of the adsorption of mixtures of carbon monoxide and hydrogen on a nickel–chromium catalyst under the conditions preceding the start of catalysis[28] shows that hydrogen is adsorbed on nickel chiefly in the form of molecules. The almost complete absence of atomic hydrogen in the synthesis of hydrocarbons was demonstrated by Craxford and Rideal[25]; the absence of dissociative adsorption of hydrogen was also noted for nickel with ethylene present in the gas[93]. Thus hydrogen is adsorbed in the form of molecules both under the conditions of formation of methane and also apparently in the synthesis of hydrocarbons on nickel, cobalt, and possibly iron catalysts. The fact that dissociation of the hydrogen molecules does not take place during adsorption on these metals is due to the influence of the adsorbed carbon monoxide. The electronic state of the catalyst surface, and hence its adsorption properties, change in such a way that there is a decrease in the energy of the bonding between the hydrogen molecules and the surface, so that decomposition of the molecules to form atoms does not take place. The adsorption of hydrogen on the nickel–chromium catalyst is accompanied by the formation of a negatively charged layer of chemisorbed gas [H_2^-] on the surface[65], due to the presence of dissolved hydrogen in the contact catalyst. These regular features of the adsorption of hydrogen are apparently preserved under the conditions

of the synthesis of higher hydrocarbons, since the catalysts for the synthesis always contain dissolved hydrogen.

In the synthesis of methane, and also apparently in the synthesis of higher hydrocarbons, carbon monoxide is adsorbed in the form of molecules with the production of a linear form of bond between the chemisorbed species and the surface atoms of the nickel; the chemisorbed layer of $[CO^+]$ is positively charged[65].

The oppositely charged adsorbed molecules of hydrogen and carbon monoxide interact in the adsorption layer. The primary products of this interaction may be adsorption complexes of the type corresponding to the enol form of formaldehyde; the existence of these complexes on metallic contact catalysts of the iron group can be taken as established. The formation of these complexes $[HCOH^+]$ takes place at a high rate[28] and is accompanied by a decrease in the work function[65]. The rate of their formation limits the rate of the catalytic conversion of carbon monoxide into methane. This is confirmed not only by the results of the measurement of the contact potential difference[65] but also, in particular, by the results of a kinetic study of the reaction in the presence of a nickel–chromium contact catalyst[57], since the rate of formation of the complexes at 75°[28] almost coincides with the hypothetical rate of the catalytic process at this temperature. In the subsequent stage, the oxygen-containing complexes apparently react in the adsorption layer with hydrogen molecules, to produce methylene radicals and water. In subsequent changes, the methylene radicals may undergo either polymerisation with the formation of hydrocarbon chains or hydrogenation to form methane.

These regular features of the mechanism of the conversion of carbon monoxide into methane on a nickel–chromium catalyst are apparently general in character and are observed in the synthesis of hydrocarbons on nickel, cobalt, and possibly iron catalysts.

Thus the following is the most probable scheme for the mechanism of the reduction of carbon monoxide to methane on these catalysts[28,65]:

1. $[\ ] + e + H_2 \rightarrow [H_2]^-$
2. $[\ ] + CO \rightarrow [CO]^+ + e$
3. $[CO]^+ + [H_2]^- \rightarrow [HCOH]^+ + e$ (slow stage)
4. $[HCOH]^+ + [H_2]^- \rightarrow [CH_2] + H_2O + [\ ]$
5. $[CH_2] + [H_2]^- \rightarrow CH_4 + e + [\ ]$†

For the synthesis of higher hydrocarbons, the fifth stage of this scheme should reflect not the reaction of methylene radicals with hydrogen, but their polymerisation.

III. MECHANISM OF THE FORMATION OF METHANE FROM CARBON DIOXIDE AND HYDROGEN

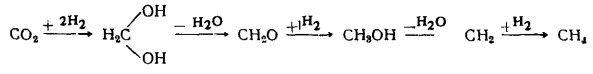
The mechanism of the hydrogenation of carbon dioxide, unlike that of the reduction of carbon monoxide, has been very little studied, although the study of the behaviour of carbon dioxide in its reaction with hydrogen is necessary for carrying out the catalytic purification of technological gases—a problem whose importance has been increasing recently. Moreover, the study of the mechanism of the synthesis of methane from carbon dioxide, in view of the high selectivity of the process, is of undoubted theoretical interest and makes it possible to develop more penetrating ideas regarding the nature of the hydrogenation of carbon monoxide.

Two proposed schemes for the mechanism of the synthesis of methane from carbon dioxide and hydrogen have been discussed in the literature. One of these was proposed by Bahr[94], who considers, on the basis of experimental data, that in the presence of Fe–Cu, Cu–Cr_2O_3, and Co–Cu–ZnO contact catalysts the reduction of carbon dioxide to methane is accompanied by the intermediate formation of carbon monoxide. This view is supported by research workers who have studied the hydrogenation of carbon dioxide on ruthenium contact catalysts[95] and in the presence of catalysts based on metals of the iron group and on various binary systems[96–100].

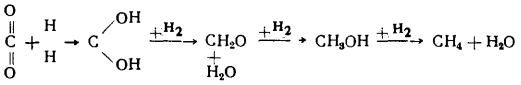
A number of facts, however, cast doubt on the correctness of Bahr's ideas. If the hydrogenation of carbon dioxide were accompanied by the intermediate formation of carbon monoxide, it might be possible under certain conditions to obtain higher hydrocarbons from CO_2, yet the hydrogenation of carbon dioxide on metallic contact catalysts of the iron group, unlike the reactions of carbon monoxide, are characterised by a high selectivity. Thus it has been shown[98,101–105] that in the presence of nickel and cobalt catalysts carbon dioxide is converted only into methane, and the formation of a small quantity of higher hydrocarbons was detected only in some instances, when mixed iron–cobalt[97] and copper–cobalt[98] contact catalysts were used. This must be due to a difference in the mechanisms of the hydrogenation of these oxides. Carbon dioxide is apparently hydrogenated to methane without the intermediate formation of carbon monoxide. Evidence in support of this is also provided by the behaviour of carbon monoxide and dioxide when these are present together in the gas. In a study of the hydrogenation of the oxides of carbon on nickel contact catalysts, Fischer and Pichler[102] showed that carbon dioxide is not hydrogenated in the presence of carbon monoxide and does not influence the transformation of the latter. These results were subsequently confirmed[56,106].

The independent mechanism of the conversion of carbon dioxide into methane is confirmed by studies of the process in the presence of a nickel–chromium catalyst. As already noted, in the presence of this catalyst carbon monoxide begins to undergo hydrogenation only above 80°.[78] Thus if the formation of methane from carbon dioxide were accompanied by the intermediate formation of carbon monoxide, it would not be observed below the temperature of the start of the hydrogenation of CO. It has been established[107], however, that carbon dioxide is hydrogenated at an appreciable rate even at 70° and below.

The idea that carbon dioxide reacts by an independent mechanism (without the intermediate formation of carbon monoxide) was reflected in a hypothesis put forward by Medsforth[108], who proposed the following scheme for the formation of methane from carbon dioxide:



Later, Medsforth's scheme was developed in detail by Pichler[109], who suggested that the hydrogenation of carbon dioxide takes place with atomic hydrogen present on the surface of the contact catalyst. According to Pichler, the reaction of carbon dioxide is described as follows:



† The symbol [ ] denotes a vacant active centre on the catalyst surface. The symbols in square brackets represent adsorbed species.

Bahr's theory[94], and the theories of Medsforth[108] and Pichler[109], start from the assumption that carbon dioxide is adsorbed on the surface of the contact catalyst in the initial stage of the process. This opinion is also held by other workers[56,103,110,111], who studied the kinetics of the hydrogenation of carbon dioxide to methane by static and flow methods. Thus it has been shown[56] that at various partial pressures of the reagents and with change in the total pressure from 0.1 atom to 1 atm in the temperature range 180–300° in the presence of a catalyst consisting of nickel on kieselguhr, the dependence of the reaction rate on the total pressure P is described by an equation of the Langmuir type

$$W = \frac{aBP}{1+BP},$$

where B and a are constants. In the opinion of the authors cited, hydrogen and carbon monoxide are comparatively weakly adsorbed on the surface of the contact catalyst. The heat of activation was 13.1 kcal mole^{-1}.

Binder and White[103], who studied the kinetics of the reaction in a flow system at atmospheric pressure in the temperature range 260–400° on a nickel–kieselguhr catalyst at stoichiometric H_2/CO_2 ratio and also in an excess of carbon dioxide, concluded that the rate-limiting stage of the process is the reaction between one adsorbed molecule of CO_2 and two (or four) dissociated hydrogen molecules. Although the kinetic equations effectively describe the experimental facts, this mechanism, in the opinion of the authors cited themselves, may be fictitious.

In a study of the kinetics of the hydrogenation of carbon dioxide above atmospheric pressure (up to 30 atm) in the presence of a nickel contact catalyst on kieselguhr[110], it was also suggested that four adsorbed hydrogen molecules react with one CO_2 molecule on the contact surface. The experimental results indicate that the activation energy has values in the range 13.1–13.9 kcal mole^{-1}. The authors cited[110] consider that the adsorption of CO_2 is weaker than the adsorption of hydrogen by a factor of 10–20.

In contrast to these studies, in which mixtures with a high concentration of carbon dioxide were used, other studies[111] were carried out at a very low concentration of CO_2 in the original gas (0.1%). The studies were carried out in a flow system at atmospheric pressure in the comparatively narrow temperature range 160–180°. A nickel–chromium contact catalyst obtained by reducing nickel chromate was used. The reaction rate is described by the empirical equation

$$W = k \cdot C_{CO_2}^{0.5},$$

indicating that carbon dioxide is adsorbed on the contact surface. The heat of activation was found to be 20.5 kcal mole^{-1}, which is much greater than the heat of activation given in the works cited earlier[56,110]. The discrepancy is due to the fact that one of the studies[111] was carried out on a contact catalyst which contained nickel oxides in addition to reduced nickel[112].

The theory of hydrogenation of carbon dioxide in an adsorption layer, developed on the basis of these studies, is disputed, however, and is not confirmed by work carried out by other experimental methods.

Although a number of workers[113-120] have shown that carbon dioxide is firmly bound to a clean nickel surface, the behaviour of CO_2 in the presence of hydrogen was not studied until recently. The only work in this direction was an attempt[121] to interpret the kinetic results of Binder and White[103] on the basis of a study of the separate adsorption of carbon dioxide and hydrogen at the temperatures of the synthesis. The mutual influence of the components during the adsorption of a mixture of gases, however, as shown for the example of carbon monoxide and hydrogen, may be considerable and may play a significant role in the reaction mechanism.

Despite the fact that in the absence of hydrogen the bond formed by carbon dioxide with the nickel surface is fairly strong, the CO_2 molecule is weakly bound to the surface under the conditions of the contact process. This follows from the results of kinetic studies[56,103] which indicated that carbon dioxide is bound to the contact surface. Thon and Taylor[122], however, in an interpretation of the mechanism of the hydrogenation of carbon dioxide, considered it unnecessary to assume that the CO_2 is adsorbed on the contact surface. On the basis of the idea that the active centre is a hydrogen atom chemisorbed on the catalyst, they suggested that this atom reacts with a molecule of carbon dioxide from the gaseous phase. Thus the same experimental results[56] have led research workers to different conclusions regarding the hydrogenation of carbon dioxide. It is obvious that kinetic data alone cannot confirm a particular reaction mechanism directly. For this, other independent methods are required.

A flow-circulation gradient-free method has been used[53] to study the kinetics of the synthesis of methane in the presence of a nickel–chromium contact catalyst by a procedure which makes it possible to follow directly the change in the weight of the catalyst during the reaction[123]. The kinetic results[53,58] are described by equations of first order with respect to carbon dioxide and of zero order with respect to hydrogen:

$$W = k \cdot p_{CO_2}^{1} \cdot p_{H_2}^{0}.$$

A change in the weight of the contact catalyst was not observed during hydrogenation, even at low temperatures (as far as 125°). It may therefore be assumed that under the conditions of the contact process there is no significant adsorption of carbon dioxide and the products of its transformation. This is confirmed by results[121] which showed that neither methane nor water are adsorbed on the surface of a nickel contact catalyst at the temperature of the synthesis. The results of the kinetic study were confirmed by a study[124] of the change in the contact potential difference during the hydrogenation of CO_2 on a nickel–chromium catalyst. When a mixture of hydrogen and carbon dioxide was introduced on to the untreated contact catalyst, the work function remained unchanged relative to that in an atmosphere of hydrogen. Moreover, sharp changes in the work function with change in temperature were not observed. This indicates that adsorption of carbon dioxide and the formation of complexes influencing the electronic structure of the catalyst does not take place on the surface of a contact catalyst containing dissolved hydrogen. The fact that carbon dioxide is not adsorbed on the surface of a contact catalyst containing adsorbed and dissolved hydrogen is also confirmed by direct data on the adsorption of CO_2 at 20°, [125] when the reaction rate is small[107].

Thus recent experimental results refute the suggestion that the start of the formation of methane from carbon dioxide on nickel catalysts is preceded by the adsorption of both components of the reaction, and indicate that hydrogen adsorbed on the contact surface reacts with molecules of carbon dioxide in the gaseous phase.

Since neither carbon dioxide nor the products of its transformation under the conditions of the synthesis of methane are adsorbed on the catalyst surface, the regular features of the adsorption of hydrogen under these conditions should apparently be the same as those under the

conditions of its separate adsorption on an untreated catalyst specimen. Thus under the conditions of the conversion of carbon dioxide into methane, the adsorbed hydrogen is present in the atomic state, and this surface layer has a negative charge [65].

The results of these studies show that the first stage in the reaction is not the reaction between molecules of carbon dioxide and hydrogen adsorbed on the contact surface. This introduces a significant correction into Pichler's scheme, given above. The experimental results also make it possible to introduce various other changes and refinements into this scheme.

The facts that the weight of the contact catalyst remains unchanged [53,123] and that the work function remains constant under different temperature conditions of the contact process [124] indicate that the transformation of carbon dioxide takes place either in the bulk or on the catalyst surface with a very low concentration of intermediate compounds, that is with a very low lifetime for these compounds in the adsorbed state. If, however, the complexes of the formaldehyde type (CH_2O) given in the scheme were formed on the catalyst surface, the formation of methane from CO_2 on the nickel–chromium contact catalyst could not be observed below 80°, [78] so that at these temperatures the complexes do not react, as was shown in an examination of the mechanism of the hydrogenation of carbon monoxide. Moreover, carbon dioxide is converted into methane at a lower temperature.

Although the formation of complexes of the type corresponding to the enol form of formaldehyde in the gas volume is quite possible, the hydrogenation of these complexes to methanol appears unlikely. In fact, if methanol were formed as an intermediate product in the hydrogenation of carbon dioxide, its conversion into methane should not have taken place at a lower rate than the formation of methane. The synthesis of hydrocarbons from methanol, however, takes place as a result of the reaction of CO and H_2 produced by the decomposition of the alcohol, and not by the direct transformation of methanol [36]. It therefore appears more probable that the enol complexes are converted into methylene radicals CH_2, as in the hydrogenation of carbon monoxide.

From the foregoing, the most probable scheme for the formation of methane from carbon dioxide and hydrogen appears to be one in which the formation of complexes of a type corresponding to the enol form of formaldehyde takes place initially, and in which the subsequent transformations are analogous to the stages in the hydrogenation of carbon monoxide, but with the significant difference that in the reduction of CO_2 these changes take place not on the catalyst surface, but in the volume of the gas. This probably explains the high selectivity of the process with respect to the formation of methane, since in this instance neither condensation of the enol complexes nor polymerisation of methylene groups can apparently take place.

For an understanding of the mechanism of a catalytic process, it is of considerable importance to determine the composition and structure of the intermediate compound, whose rate of formation determines the observed reaction rate. In accordance with the scheme being considered, it is assumed that the limiting stage of the process involving the conversion of carbon dioxide into methane is the stage involving the formation of the dioxymethylene radical, which can be regarded as an isomer of formic acid.

Golodets and Roiter [126] showed that evidence in support of the proposed composition and structure of an active complex is provided by agreement between the thermodynamic characteristics of the activated complex, such as the heat and entropy of activation calculated from kinetic data, and the values of these quantities calculated approximately for the assumed activated complex.

Analysis of the experimental entropy of activation of the hydrogenation of carbon dioxide on a nickel–chromium catalyst [56] showed that the first stage of the reaction apparently does involve the formation of dioxymethylene radicals, and that the rate of this stage determines the overall rate of the process.

On the basis of the foregoing, the mechanism of the hydrogenation of carbon dioxide is most probably represented by the following scheme [56,124]:

1. $2[\ ] + 2e + H_2 \rightarrow 2[H]^-$
2. $2[H]^- + CO_2 \rightarrow [HCOOH] \rightarrow 2[\ ] + C(OH)(OH) + 2e$ (slow stage)
3. $C(OH)(OH) + H_2 \rightarrow H{-}C{-}OH + H_2O$
4. $H{-}C{-}OH + H_2 \rightarrow CH_2 + H_2O$
5. $CH_2 + H_2 \rightarrow CH_4$ ‡

According to this scheme, the process is initiated by the activation of only the hydrogen on the catalyst surface, after which the reaction takes place in the gas volume.

The proposed scheme agrees with the experimental results of the study of the process on a nickel–chromium catalyst, within the limits of the sensitivity of the methods of study. It may be of general significance for the synthesis of methane in the presence of catalysts based on nickel. Evidence in support of this is indicated by the fact that the same value is obtained for the heat of activation (13.1–13.9 kcal mole^{-1}) in studies of the kinetics of the process at extremely low (as far as 0.4%) concentrations of carbon dioxide [53] and at concentrations close to the stoichiometric ratio at atmospheric pressure [56] and at pressures up to 30 atm [110]. From this it follows that over a wide range of partial pressures, carbon dioxide does not react with the contact surface and the same mechanism is observed for the synthesis of methane.

IV. HYDROGENATION OF CARBON MONOXIDE AND DIOXIDE PRESENT TOGETHER IN THE GAS PHASE

A knowledge of the mechanism of contact reactions makes it possible not only to explain the observed kinetic features but also to predict the possibility of carrying out these reactions in other more complex examples. In this connection it is appropriate to examine data on the synthesis of methane from carbon monoxide and dioxide on the basis of theories of the mechanisms of the transformation of these oxides.

The transformation of carbon monoxide and dioxide on nickel catalysts has been studied [56,102,106]. It was established that CO_2 is not hydrogenated in the presence of carbon monoxide and does not influence the transformation of CO. Nicolai and coworkers [56], in particular, considered that the oxides of carbon are hydrogenated according to their adsorbability. Since in the presence of hydrogen, carbon monoxide is adsorbed more strongly than CO_2, the authors cited assumed that in the presence of adsorbed CO, adsorption of carbon dioxide is impossible, so that the surface reaction of CO_2 with hydrogen is impossible. This view is incorrect, however, since under the conditions of the hydrogenation of CO_2, carbon dioxide is not adsorbed, even in the absence of carbon monoxide.

‡ See footnote to page No. 733.

The results obtained by Nicolai and coworkers[56] were also discussed by Thon and Taylor[122], who suggested that the active centre is a hydrogen atom adsorbed on the catalyst surface. When carbon monoxide and dioxide are present in the gas under the conditions of the hydrogenation, the CO and CO_2 compete for these active centres. Since the carbon monoxide molecules react more rapidly with the active centres under these conditions, the CO is hydrogenated, and not the carbon dioxide. This suggestion cannot be correct, however, since the mechanism of the transformation of carbon monoxide is different from that of the hydrogenation of carbon dioxide.

A difference in the behaviour of carbon monoxide and dioxide was observed in a study of the hydrogenation of their mixtures on a nickel–chromium catalyst in a large excess of hydrogen at various concentrations of the oxides of carbon in the gas[127]. Under these conditions, as in the process at high concentrations of the oxides of carbon[56,102,106], the rate of hydrogenation of carbon monoxide is independent of the presence of carbon dioxide in the gas. Observation of the change in the weight of the catalyst in addition to kinetic studies showed that the increase in weight corresponds to the values observed for the hydrogenation of carbon monoxide in the absence of CO_2. From this it follows that when the oxides of carbon are present together in the mixture with hydrogen, only the processes involving the transformation of the carbon monoxide take place on the contact surface. Hydrogenation of carbon dioxide does not take place at all over a wide range of CO concentration. These results indicate that carbon monoxide is a powerful poison for the hydrogenation of CO_2 on nickel catalysts.

These ideas regarding the mechanisms of the formation of methane from carbon monoxide and dioxide enable the kinetic features of the hydrogenation of mixtures of these oxides to be explained in terms of the influence of adsorbed carbon monoxide on the position of the equilibrium for the dissociation of molecular hydrogen adsorbed on the catalyst surface:

$$[H_2] \rightleftarrows 2[H] .$$

The presence of carbon dioxide in hydrogen has no influence on the electronic state of the catalyst surface, and hence on its adsorption properties. In this instance the equilibrium is displaced to the right, that is the hydrogen is adsorbed chiefly in atomic form, which is active with respect to the carbon dioxide present in the gaseous phase.

In the presence of hydrogen, carbon dioxide is not adsorbed on nickel. Carbon monoxide is readily chemisorbed on the contact surface and alters its properties: when carbon monoxide is present, the equilibrium for the dissociation of H_2 is displaced to the left, and hydrogen is adsorbed on the nickel surface chiefly in the form of molecules, that is in a form which is active with respect to adsorbed CO molecules but is not capable of reacting with CO_2 molecules from the gaseous phase.

Thus the poisoning of the catalyst, by carbon monoxide, with respect to the hydrogenation of CO_2 is not due to simple blocking of the active centres by carbon monoxide. Similarly, it cannot be regarded as a result of competition between the molecules of carbon monoxide and dioxide for the active regions of the surface. This phenomenon results from differences in the mechanisms of the hydrogenation of the oxides of carbon, and the poisoning influence of adsorbed carbon monoxide is not a direct influence, but results from a change in the electronic state of the catalyst, leading to the production of forms of adsorbed hydrogen which are unable to reduce CO_2.

It is only at a very low concentration of carbon monoxide, when its hydrogenation takes place under external transition conditions, that the concentration of atomic hydrogen on the nickel surface becomes sufficient for the rate of transformation of carbon dioxide to become appreciable, and this is in fact observed[127]. The equilibrium for the dissociation of molecular hydrogen is apparently displaced considerably to the right in those instances when the formation of methane from carbon monoxide takes place in the range of external diffusion and the concentration of CO on the contact surface is close to zero, so that the carbon monoxide cannot alter the properties of the surface significantly.

Thus the possibility of carrying out the reduction of carbon dioxide in the presence of carbon monoxide is determined by the macro-kinetic features of the transformation of the latter.

This conclusion has a number of consequences, which may be of practical importance for the fine catalytic purification of gases from oxides of carbon by transformation into methane.

The purification of gases from oxides of carbon obviously must be carried out in the range of external diffusion with respect to CO. It is only under these conditions that the degree of transformation of carbon dioxide achieved is the same as that in the absence of carbon monoxide and that most complete removal of traces of both substances from the gas can be effected. This agrees with the results of a study[128] of the purification of a nitrogen–hydrogen mixture from oxides of carbon on a nickel–chromium catalyst.

Carbon monoxide is a powerful poison with respect to the hydrogenation of many substances, particularly unsaturated compounds, on nickel. In a number of contact processes, for example the hydrogenation of ethylene, benzene, and phenol, carbon dioxide is not a catalyst poison. In these instances the removal of carbon dioxide from the hydrogen used for the hydrogenation is not necessary, whereas purification from carbon monoxide is required. This selective removal of carbon monoxide can be carried out under the conditions of hydrogenation in the external transition range, when almost no hydrogenation of carbon dioxide takes place. The possibility of carrying out the purification in this way has been demonstrated[129]. It should, however, be noted that these conditions can be used only when very thorough purification of the gas from carbon monoxide is not required.

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Examination of the mechanism of the synthesis of methane from carbon monoxide and hydrogen indicates that the most probable reaction scheme is that proposed by Eidus. The accumulated data obtained by various methods make it possible to establish the reactive forms of the adsorbed molecules and the signs of their charges, and also to demonstrate fairly reliably the existence of chemisorbed complexes of a type corresponding to the enol form of formaldehyde. Strong evidence in support of their existence is provided by information obtained from the infrared spectra of the surface compounds. Success in these studies, however, requires the accumulation of these complexes in sufficient concentration. This may be achieved by carrying out the reaction of the adsorbed molecules of carbon monoxide and hydrogen under the conditions immediately preceding the catalytic action and, in view of the low rate of formation of the complexes, when the process has proceeded for a sufficient length of time.

The mechanism of the synthesis of methane from carbon dioxide and hydrogen differs significantly from the mechanism of the reduction of carbon monoxide.

The mechanism of the poisoning action of carbon monoxide, demonstrated for the example of CO_2, may be of general importance for finding the most rational solution to the problem of carrying out the important industrial processes involved in the hydrogenation of organic substances (benzene, phenol, ethylene, etc.), where it is known that the presence of carbon monoxide in the synthesis gas poisons the catalyst. In these instances, hydrogen is subjected to thorough purification to remove carbon monoxide. If the concentration of carbon monoxide in the original gas is such that under the conditions of the hydrogenation of the organic substances the reduction of CO takes place under external diffusion conditions, however, preliminary purification of the hydrogen from CO apparently is not required.

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Pisarzhevskii Institute of
Physical Chemistry,
Academy of Sciences of
the Ukrainian SSR, Kiev

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Experimental Determination of the Dipole Moments of Organic Molecules in Excited Electronic States†

N.G.Bakhshiev, M.I.Knyazhanskii, V.I.Minkin. O.A.Osipov, and G.V.Saidov

Modern experimental methods for the determination of dipole moments of organic molecules in excited electronic states are reviewed in detail and their relative merits are discussed.
The principal results obtained with the aid of these methods are presented (compiled in a Table). The bibliography includes 88 references.

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I. INTRODUCTION

The properties of excited‡ molecular states as well as those of the ground state are ultimately determined by the distribution of electron density in the molecule. From this point of view, it is of interest to determine the dipole moments of the molecule in excited states, since the magnitude and orientation of the dipole moment relative to the molecular framework are directly related to the distribution of electron density in the corresponding eigen state. Comparison of the dipole moments in the ground ($\vec{\mu}_g$) and excited ($\vec{\mu}_e$) states makes it possible to infer the nature of the changes in electron density at individual groups of atoms in the molecule following excitation, which is of particular interest for the determination of the reaction centre in the excited state of the molecule undergoing a photochemical reaction and also for the understanding of the relation between the migration of the charge and the redistribution of electron excitation energy. The latter in turn is closely related to various non-radiative deactivation processes and hence to the capacity of the compound for luminescence. Furthermore, the use of the experimental dipole moments of excited states may facilitate a more soundly based choice of parameters in quantum-mechanical calculations of various physicochemical properties of molecules.

Unfortunately $\vec{\mu}_e$ cannot be determined experimentally by the usual methods for the measurement of electrical polarisation, since the lifetime of the excited states is extremely short so that even under intense irradiation this factor makes it difficult to establish an equilibrium concentration of excited molecules sufficiently high for the measurement of electrical polarisation. At the same time, since one is dealing with the optical excitation of the molecule, the method for the determination of the dipole moments of excited states must clearly be spectroscopic. Consequently it is necessary to establish a relation between the principal spectroscopic parameters of the molecule [the energy (frequency) and probability (intensity) of the electronic transition], on the one hand, and the electric dipole moments characteristic of the molecule in the ground and excited states, on the other.

In the last 10–12 years a number of methods for the experimental determination of the moment $\vec{\mu}_e$ have been proposed. It is significant that these methods differ sharply from one another in the nature of the physical phenomena on which they are based and consequently in the spectroscopic parameters which are measured. However, despite the urgency of the problem, so far there has been no adequate review of these methods. The reviews known to the authors[1,2] are extremely short, do not give a complete idea of the available methods and their modifications, and many important results are omitted. The present review probably includes most of the studies (up to 1967) in which the dipole moments of molecules in excited states were measured or estimated experimentally. The principal formulae used to determine the dipole moments are presented in a form convenient for direct practical use—achieved as a result of a number of assumptions which have been justified in practice. At the end of the review there is a Table which presents the principal data on the dipole moments $\vec{\mu}_e$ of a number of molecules and complexes obtained to date.

The methods for the determination of dipole moments which have been fairly widely adopted recently can be usefully combined into the following four groups.

1. The method of spetral shifts, based on the study of the displacements of the frequencies of electronic transitions in the electric field of intermolecular forces and consisting in the analysis of the shifts of the absorption and luminescence bands under the influence of a solvent.

2. The method of electrical polarisation of fluorescence. Here the degree of polarisation of the emission by solutions of the test substances in a powerful electric field is measured, i.e. ultimately the anisotropy of the emission in the direction of the field orienting the molecules is investigated.

3. The method of electrical dichroism. Here the dichroism of the absorption by molecules in a solution placed in a powerful electric field is studied, i.e. the anisotropy of absorption in the direction of the orienting field is considered.

4. The method based on the investigation of the splitting of the fine rotational structure of the absorption bands of

†This paper is an expanded version of the report delivered at the First All-Union Conference on Dipole Moments and Molecular Structure at Rostov-on-Don in 1967.

‡Only excited electronic states are considered here.

certain molecules in the gas phase in a powerful electric field (the Stark effect, which includes not only the excited electronic states but also the ground state).

It must be emphasised yet again that all the methods enumerated above are spectroscopic and require that the test molecule be acted upon by electric fields (external or intermolecular). It should also be noted that all the methods are based on definite model hypotheses concerning the interaction of the molecule with the medium (the Onsager theory, Debye's theory of orientation polarisation, etc.). Each group of methods will be discussed in greater detail.

II. METHOD OF SPECTRAL SHIFTS

The determination of the dipole moments of excited states by the methods of spectral shifts is based on the study of solvatochromism—the displacement of the bands in electronic absorption and emission spectra of the test molecules under the influence of a solvent. The phenomenon of solvatochromism arises from the difference between the energies of the interaction of the molecule with the medium in different electronic states, which is in turn determined by the change in the physicochemical properties (in particular the dipole moment) of the molecule on optical excitation. The fundamental postulates concerning the relation between the parameters characterising the system "test molecule–solvent" and the displacement of the spectra in solution relative to those in the gas phase were described for the first time by Bayliss, McRae, and Ooshika [3-6]. Taking into consideration the equilibrium (eq) and Franck–Condon (F–C) levels in the ground (g) and excited (e) states (Fig. 1), the authors calculated, using second-order perturbation theory, the stabilisation energy of the dissolved molecule (i.e. the energy of its interaction with solvent molecules) in various states. Account was taken of different types of van der Waals interaction (orientation, inductive, and dispersion), while specific interactions of donor–acceptor type were disregarded.

To derive the final expression relating the experimental band shifts to the characteristics of the molecule and the medium, use is made of the Onsager model [7], according to which the molecule is treated as a point dipole in a spherical cavity with radius a (the Onsager radius) within the solvent which is treated as a homogeneous continuous medium with a dielectric constant ϵ and refractive index n. The point dipole interacts with the "reactive" field arising as a result of the orientation-inductive polarisation of the solvent molecules under the influence of the dissolved molecule. The general treatment of the problem [4-6] leads to very complex expressions containing terms each of which describes a particular type of interaction between the molecule and the solvent. These formulae cannot be used directly to determine dipole moments, since they contain a large number of parameters which have not been determined and cannot be determined experimentally. However, with certain assumptions made by McRae (in particular it is assumed that the molecular polarisibility α does not change on excitation, i.e. $\alpha_e = \alpha_g$), it is possible to obtain a fairly simple formula for the frequency shift of a purely electronic absorption transition in polar solvents:

$$\Delta\nu_a = (AL_0 + B)\frac{n_D^2-1}{2n_D^2+1} + C\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n_D^2-1}{n_D^2+2}\right], \qquad (1)$$

where A, L_0, B, and C are constants characterising both the solvent and the solute molecule and $C = (2/hca^3)$: $:(\vec{\mu}_g - \vec{\mu}_e)\vec{\mu}_g$. Here h is the Planck constant, c the velocity of light in a vacuum, n_D the refractive index of the solvent corresponding to the sodium D-line, ϵ the static dielectric constant, a the Onsager radius, and $\vec{\mu}_g$ and $\vec{\mu}_e$ are the dipole moments of the solute molecule in the ground and excited states respectively. It should be noted that, if the shape of the band depends only slightly on the solvent, i.e. the band is displaced virtually as a whole, the shift $\Delta\nu_a$ may be determined from the position of the absorption band maximum.

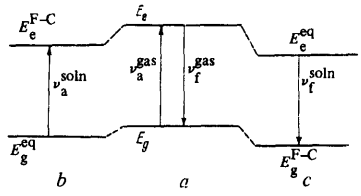

Figure 1. Schematic representation of the electronic levels of a molecule in the gas phase and in solution (ground and first excited states): *a*) absorption and emission (gas); *b*) absorption (solution); *c*) emission (solution).

McRae used Eqn. (1) to estimate $\vec{\mu}_e$ of Phenol Blue having investigated the shifts in the absorption spectra in 21 solvents. The constants A, L_0, and B were determined very approximately from additional experimental data and on the basis of different postulates. Using the known value $\vec{\mu}_g \simeq 5.8$ D and assuming that $\alpha \simeq 4$–5 Å and $\vec{\mu}_g \| \vec{\mu}_e$, McRae estimated $|\mu_e|$ for Phenol Blue to be 7.5–9.1 D and noted that, although this value is of the expected order of magnitude, it does not constitute a significant confirmation of a considerable contribution of the dipolar structure to the excited state of the molecule investigated.

The work of Lippert [8-11], who proposed a method for the determination of μ_e of the first singlet excited state of fluorescing polar molecules, which is significantly higher than μ_g, played an important role in the development of a method for the measurement of the dipole moments of excited molecules. This method is based on the application of the Ooshika formula to determine the difference between the shifts of the absorption ($\Delta\nu_a$) and fluorescence ($\Delta\nu_f$) bands under conditions such that the orientation relaxation time of the solvent molecules (τ_{or}) is much less than the lifetime of the excited fluorescent state (τ_f). The following simple expression is then obtained (neglecting the small terms and the constant):

$$\Delta\nu_{a-f} = \nu_a - \nu_f = \frac{2}{hc}\left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n_D^2-1}{2n_D^2+1}\right)\frac{(\vec{\mu}_e - \vec{\mu}_g)^2}{a^3}, \qquad (2)$$

which relates the Stokes shift of the fluorescence spectrum relative to the absorption spectrum ($\Delta\nu_{a-f}$), to the characteristics of the molecule and the medium. Here ν_a and ν_f are the frequencies of the absorption and fluorescence band maxima respectively and the significance of the remaining quantities is clear from the preceding description. The measurement of ν_a and ν_f in a set of polar and non-polar ($\epsilon = n_D^2$) solvents makes it possible to calculate

μ_e, using specified values of μ_g and a, under the condition $\vec{\mu}_e \| \vec{\mu}_g$ by means of the simple formula

$$\mu_e = \mu_g \pm 0.001\sqrt{ma^3},$$

m being found from a plot of the relation $\Delta\nu_{a-f} = m\Delta f$, where

$$\Delta f = \left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n_D^2 - 1}{2n_D^2 + 1}\right].$$

The method described was used by Lippert [8-11] to determine the dipole moments μ_e of a number of molecules, in particular stilbene derivatives assuming that $a \sim 0.8\rho$, where ρ is the radius of the smallest sphere enclosing the molecule.

The disadvantages of Lippert's method consist mainly in the failure to take into account the capacity of the molecule to be polarised in an electric (and in particular in a reactive) field and also there is the following important defect: namely, having restricted the treatment to the analysis of the Stokes shift $\Delta\nu_{a-f}$, Lippert [8-11] in fact fails to realise the additional possibilities [compared with formula (1) for example] associated with the independent measurement of both absorption and fluorescence bands. As a result, the experimenter has at his disposal, as in the case of Eqn. (1), only one experimentally measured spectroscopic parameter ($\Delta\nu_{a-f}$) instead of two ($\Delta\nu_a$ and $\Delta\nu_f$), which considerably reduces the effectiveness of the method.

Independently of Lippert, Mataga and coworkers [12-16] also obtained Eqn. (2) on the basis of the Ooshika formula and, having analysed it in detail and compared it with experimental data, concluded, in agreement with Lippert [8-11], that it is possible to determine the difference between the dipole moments of molecules in the ground and excited states from the changes in the Stokes shift $\Delta\nu_{a-f}$ due to orientation interactions. No hypotheses concerning the relative orientation of the moments $\vec{\mu}_g$ and $\vec{\mu}_e$ or the values of μ_g have been put forward by Mataga and coworkers [12-16] and only the values of $|\Delta\vec{\mu}|$ are considered.

Comparison of the experimental and theoretical values makes it possible in some cases to estimate the applicability of a particular method for the calculation of charge distribution in the excited molecule (for example for naphthols, naphthylamines, and carbazole [13,14] and also aniline [17]) and to arrive at certain conclusions concerning the structure of the molecule in the excited state. Molecular excitation is accompanied, according to Mataga's data, by a considerable increase of the dipole moment, which is associated with charge transfer from electron-donor substituents along the conjugated bond chain. It has been established that in α-naphthylamines the increase of the dipole moment on excitation is greater (4.4 D) than in the corresponding β-derivatives (3.5 D), while the values of $|\Delta\vec{\mu}|$ for naphthols are considerably lower (0.5–1 D) than for naphthylamines and the sequence of the changes $|\Delta\vec{\mu}|$ for α- and β-derivatives is reversed.

A rough estimate shows [12-16] that $|\Delta\vec{\mu}|$ for isomeric aminobenzoic acids increases on going from *ortho*- to *meta*-isomers. The quantity $\delta = |\Delta\mu|^2/a^3$, determined from Eqn. (2), is $\delta = 7500$ cm^{-1} for *NN*-dimethyl-α-naphthylamine. This suggests that the $N(CH_3)_2$ group rotates about the C–N bond during the lifetime of the excited state [16]. The authors believe [16] that such rotation becomes possible as a result of charge transfer from the nitrogen to the π-electron system of naphthalene on electronic excitation.

The work of Ito et al. [18], where an attempt was made to measure the change in dipole moments on $n-\pi^*$ excitation of ketone molecules, is of interest. The authors used the McRae formula [5], in which a small term, characterising the so called quadratic Stark effect, was omitted:

$$\Delta\nu_a = \text{dispersion term} + B\frac{n_D^2 - 1}{2n_D^2 + 1} + C\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n_D^2 - 1}{n_D^2 + 2}\right], \quad (3)$$

$$B = \frac{1}{hc}\cdot\frac{\mu_g^2 - \mu_e^2}{a^3}, \quad (4)$$

$$C = \frac{2}{hc}\frac{\vec{\mu}_g(\vec{\mu}_g - \vec{\mu}_e)}{a^3} \quad (5)$$

(the notation is the same as above). Since according to Eqns. (4) and (5) it is necessary to determine experimentally either the parameter B or C in order to find μ_e, Ito et al. [18] proposed two versions of the method.

The first version is based on the measurement of the shifts $\Delta\nu_a$ in non-polar solvents with different refractive indices (n_D) (for example hexane, carbon tetrachloride, dioxan§, benzene). For such solvents ($n_D^2 \simeq \epsilon$), the following equation should hold:

$$\Delta\nu_a = \text{dispersion term} + B\frac{n_D^2 - 1}{2n_D^2 + 1} + \text{const.} \quad (6)$$

It has been established experimentally [18] that, for all the compounds investigated, except acetone, the dispersion interaction may be neglected and the following linear relation may be employed:

$$\Delta\nu_a \simeq B\frac{n_D^2 - 1}{2n_D^2 + 1} + \text{const.} \quad (7)$$

The authors confine themselves to the determination of the sign of B only. Since $B > 0$ ("blue" shift of the absorption band), it follows that $\mu_e < \mu_g$, i.e. on $n-\pi^*$ excitation the dipole moment falls.

In the second version of the method the difference between the positions of the absorption band maxima in two polar solvents with approximately the same values of n_D but different ϵ is measured. In such solvents the dispersion terms and the term involving $(n_D^2 - 1)/(2n_D^2 + 1)$ do not change, so that the difference between the frequencies at the band maxima is described by the simple formula

$$\nu_1 - \nu_2 = C\left(\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} - \frac{\varepsilon_2 - 1}{\varepsilon_2 + 2}\right). \quad (8)$$

Ethyl ether and acetonitrile ($n_D = 1.356$ and 1.344 respectively), for example, may be used as solvents. The absorption spectra of these solvents are similar and do not contain intense bands above 2000 Å, which ensures approximate equality of the dispersion terms in Eqn. (3). [5] The dielectric constants ϵ of these solvents differ sharply (4.34 for ether and 37.50 for acetonitrile), which permits the variation of ϵ¶ of their mixtures over a wide range. By measuring ν_a for solutions in each mixture of this kind, it is possible to test the validity of Eqn. (8) and, if it holds, to determine the parameter C and hence μ_e for known values of μ_g and a. The measurements carried out in this way enabled Ito et al. to estimate the dipole moments μ_e of acetophenone on $n-\pi^*$ excitation as 0.5 D ($a \simeq 4.0$ Å). For the remaining ketones investigated by the authors the corresponding values of μ_e do not exceed 0.5 D. Then in all cases μ_e is less than μ_g approximately by 3 D. Using

§However, dioxan behaves in the majority of cases as a polar solvent and does not obey Eqn. (6).

¶The dielectric constant ϵ of the mixture of solvents may be calculated from the formula $\epsilon = \epsilon_0 + bw$, where ϵ_0 is the dielectric constant of ether, b the difference between the dielectric constants of acetonitrile and ether, and w the weight fraction of acetonitrile in solution.

the same method, Semba [19] observed an increase in the dipole moment of nitrobenzene derivatives on excitation in the long-wavelength region and determined the dipole moment of the first singlet state of the *p*-nitroanisole molecule (for $a \simeq 4$ Å and $\mu_g \simeq 5$ D, the dipole moment is $\mu_e \simeq 7$ D).

The version of the McRae method described is very convenient for the estimation of μ_e of sparingly soluble non-fluorescent compounds, but it requires a very cautious approach and tests in each individual case, since the McRae theory, developed for two-component solutions cannot be formally extended to mixtures of two solvents, i.e. to three-component solutions [20].

Gosavi and Rao [21] used Eqn. (8) to determine the dipole moments of the $n-\pi^*$ excited states of thiourea derivatives from the shifts of the $n-\pi^*$ absorption band maximum in ether and acetonitrile without using a mixture of solvents.

Baba et al. [22] applied the McRae formula [Eqn. (3)] and analysed the shifts of the fluorescence spectra. The authors calculated the relative shifts of the absorption ($\delta\nu_{abs}$) and fluorescence ($\delta\nu_{fl}$) bands for various solvents with the same values of n and dispersion terms but different ϵ. Then one obtains for absorption

$$\delta\nu_{abs} = \Delta\nu_{2abs} - \Delta\nu_{1abs} = \frac{2}{hc}\frac{\vec{\mu}_g(\vec{\mu}_e - \vec{\mu}_g)}{a^3}\left(\frac{\varepsilon_2 - 1}{\varepsilon_2 + 2} - \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\right)$$

and for fluorescence

$$\delta\nu_{fl} = \Delta\nu_{2fl} - \Delta\nu_{1fl} = \frac{2}{hc}\frac{\vec{\mu}_e(\vec{\mu}_e - \vec{\mu}_g)}{a^3}\left(\frac{\varepsilon_2 - 1}{\varepsilon_2 + 2} - \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\right),$$

where $\Delta\nu$ are the shifts of the absorption and fluorescence bands in the corresponding solvents (1 and 2) relative to the spectra of the vapour. Hence, under the condition $\vec{\mu}_e \parallel \vec{\mu}_e$, we have

$$\frac{\mu_e}{\mu_g} = \frac{\delta\nu_{fl}}{\delta\nu_{abs}}. \qquad (9)$$

Using acetonitrile and ether and also other solvents [23] with similar n_D, Baba et al. [22] calculated the dipole moment μ_e for $n-\pi^*$-fluorescent states of pyridazine, pyrimidine, and pyrazine [22] and also 9,10-diazaphenanthrene [23]. They found that the dipole moments of pyridazine, 9,10-diazaphenanthrene, and pyrimidine decrease significantly on $n\pi^*$ excitation (by factors of 3.6, 3.4, and 4.2 respectively) and the sign of the dipole moment of pyrimidine is reversed. The authors suggest that these changes are associated with the transition of the sp^2-hybridised n electrons of nitrogen to the π orbital. At the same time for pyrazine $\mu_e \simeq \mu_g \simeq 0$ due to the symmetrical positions of the hetero-atoms.

The method employed by Baba is attractive because in the calculations it is unnecessary to specify the Onsager radius, the value of which usually involves a considerable error. At the same time the exclusive use of solvents with refractive indices n_D which differ only slightly and the assumption that the moments $\vec{\mu}_g$ and $\vec{\mu}_e$ are parallel greatly restricts the scope of the method.

The McRae formula enabled Robertson et al. [24] to estimate the dipole moments of certain excited states (^1L_b, ^1L_a, and ^1B_b) of azulene. The authors demonstrated experimentally the validity of the assumptions underlying the McRae formula [Eqn. (1)] and showed that $AL_0 + B = K$ is constant for the entire series of solvents which they employed. The constant K for the series of solvents (hexane, heptane, pentane, etc.) was determined from the formula $\Delta\nu_a = K(n^2 - 1)/(2n^2 + 1)$ by least squares. In turn, the constant $C = (2/hc)\mu_g(\mu_g - \mu_e)/a^3$ was calculated from the absorption bands shifts in polar solvents so as to obtain best agreement between the calculated and observed shifts $\Delta\nu_a$. The data for alcohols are excluded, since in this case hydrogen bonds may have a significant effect, which is not taken into account by the McRae formula [Eqn. (1)]. The values of $\vec{\mu}_e$ for molecules in the above three excited states were determined for two Onsager radii, $a \simeq 3$ and $a \simeq 4$ Å, and the results obtained were compared with those of the theoretical calculations of Pariser. The authors state that best agreement between the calculated and experimental moment $\vec{\mu}_e$ in the state ^1L_b is achieved with $a > 4$ Å. For the remaining states, the agreement is less satisfactory.

In a study based on the McRae theory and the formula for the shift of the electronic spectra under the influence of the solvent derived by Liptay [26], Beens and Knibbe [25] determined from fluorescence spectroscopic data alone the dipole moments of certain molecular charge-transfer complexes in the excited state. They assumed that $\vec{\mu}_e \parallel \vec{\mu}_g$ and that the Onsager radius $a \simeq 5$ Å. According to these measurement, the dipole moment in the excited state proved to be 10 D, which is consistent with the hypothesis of charge transfer on excitation. Liptay [27] determined the dipole moment of aniline as $\mu_e = 6$ D.

In contrast to these investigations, Kosower [28] attempted to estimate the dipole moment of the excited state without using any previously derived relations. He determined the stabilisation energy ΔE_e of the excited $\pi-\pi^*$ state of the mesityl oxide molecule in water from the shift of the absorption spectra of the aqueous solution relative to the spectrum in iso-octane (it was assumed that in this non-polar solvent the position of the absorption band of the test molecule is the same as in the spectrum of the gaseous compound). The molecular complex of iodine with 1-ethyl-4-methoxycarbonylpyridine ($\mu_g = 13.90$ D; $\Delta E_g = 17.3$ kcal mole^{-1}) was chosen as standard and it was assumed that the stabilisation energy is proportional to the dipole moment; then, according to the authors estimate, $\mu_e \simeq 7.6$ D for mesityl oxide. The lower limit of the dipole moment of Phenyl Blue in the excited state was estimated similarly as 10.2 D, which exceeds the value obtained by McRae [5]. However, this approach to the determination of μ_e cannot be regarded as adequately justified.

The additional possibilities mentioned above, associated with the independent investigation of the shift of the absorption ($\Delta\nu_a$) and fluorescence ($\Delta\nu_f$) spectra of the solutions relative to those in the gas phase, were employed by one of the authors of the present review [29-37]. The method is based on the hypothesis that the effect of solvents on the position of the electronic spectra of molecules is in general determined by intermolecular interactions of the universal van der Waals type. Using these hypotheses, the Onsager model, and general physical considerations without resorting to quantum-mechanical methods of calculation, the author obtained relatively simples expressions for the shifts of the electronic spectra as a function of n and ϵ for the solvent [29]. In the derivation of the formulae, account was taken of the polarisibility of the molecule in the ground and excited states. It is particularly important that the author dealt with the general case where the angle φ between the moments $\vec{\mu}_g$ and $\vec{\mu}_e$ is not 0° or 180°. Such treatment makes it possible to determine this angle together with the moment $\vec{\mu}_e$ from the experimental data and thereby investigate the anisotropy of the distribution of electron density in molecules on optical excitation. Subsequently the author developed a more general theory of the interaction between the solvent and the solute molecule which is valid for any relations between the orientation relaxation time τ_{or} and the lifetime

of the molecule in the excited electronic state τ_{fl}.[38] Furthermore, account was taken of the additional shift of the observed spectrum relative to the true spectrum as a result of the spectral variation of the field strength associated with a light wave acting upon the molecule in the condensed medium. The following expressions were obtained[38] for the case $\tau_{or} \ll \tau_{fl}$, which is most frequently encountered in practise:

$$hc\Delta\nu^s = C_2\left[\frac{2n^2+1}{n^2+2}\frac{\varepsilon-1}{\varepsilon+2} + p^s\frac{n^2-1}{n^2+2}\right] = C_2 f(\varepsilon, n), \quad (10)$$

$$hc\,\Delta\nu^{a-f} = \Delta C^{a-f}\left[\frac{2n^2+1}{n^2+2}\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right) + p^{a-f}\frac{n^2-1}{n^2+2}\right] = \Delta C^{a-f}\varphi(\varepsilon, n) \quad (11)$$

where $\Delta\nu^S = (\Delta\nu_a + \Delta\nu_f)/2$, $\Delta\nu^{a-f} = \Delta\nu_a - \Delta\nu_f$ (the change in the Stokes shift), and $f(\epsilon, n)$ and $\varphi(\epsilon, n)$ are the so called universal interaction functions.

The dipole moment μ_e and the angle φ between $\vec{\mu}_e$ and $\vec{\mu}_g$ are defined by the following formulae, provided that μ_g and a (the Onsager radius) are known:

$$\mu_e = \sqrt{\mu_g^2 - C_2 hca^3}\ ,$$
$$\cos\varphi = \frac{1}{2\mu_g\mu_e}\left[(\mu_g^2+\mu_e^2) - \frac{\Delta C^{a-f}}{2C_2}(\mu_g^2-\mu_e^2)\right]. \quad (12)$$

The parameters C_2 and ΔC^{a-f} are found from plots based on Eqns. (10) and (11). The auxiliary parameters p^S and p^{a-f} are determined either from the condition that the straight line must pass through the point corresponding to the vapour phase (no shift) or (if no data for the spectra in the gas phase are available) from the condition of optimum linearity of the relation investigated. In the calculation of the parameters C and p good results are obtained by the method of least squares. We may also note that, in the absence of data for the spectra in the vapour phase, one can use the results of measurements of the relative shifts of the band maxima in polar media and the formulae

$$\frac{hc}{\Delta F(n)} = C_2\frac{\Delta f(\varepsilon, n)}{\Delta F(n)} + \text{const.}, \quad (13)$$

$$\frac{hc\delta(\Delta\nu^{a-f})}{\Delta F(n)} = \Delta C^{a-f}\frac{\Delta\varphi(\varepsilon, n)}{\Delta F(n)} + \text{const.}, \quad (14)$$

where

$$\delta\nu^s = \nu_2^s - \nu_1^s; \quad \delta(\Delta\nu^{a-f}) = \Delta\nu_2^{a-f} - \Delta\nu_1^{a-f},$$
$$\Delta F(n) = \frac{n_2^2-1}{n_2^2+2} - \frac{n_1^2-1}{n_1^2+2},$$

in which subscripts 1 and 2 refer to different polar solvents. The values of μ_g and a required for the calculations by Eqn. (12) are determined from electrical measurements (or from tabulated data) and from structural models of the molecules respectively.

Apart from the case discussed above, a widely occurring important special case, corresponding to the condition $\varphi \simeq 0$ or 180°, is also of interest. Then, according to Bakhshiev's investigations[29-32], we have

$$\mu_g = \sqrt{\frac{C_2 hca^3}{1-K^2}}; \quad \mu_e = K\mu_g, \quad (15)$$

where

$$K = \pm\frac{1-\frac{\Delta C^{a-f}}{2C_2}}{1+\frac{\Delta C^{a-f}}{2C_2}}$$

(+ for $\varphi = 0$ and − for $\varphi = 180°$).

It is readily seen that, by specifying the value of a, it is possible to determine independently both μ_e and μ_g from spectroscopic data using Eqns. (15). Furthermore, it is significant that μ_e can be found in this case from the known value of μ_g without using the Onsager radius a, because the coefficient K in Eqn. (15) is determined solely by spectroscopic data. Finally, Eqns. (15) may be used for the direct experimental determination of the Onsager radius itself, which is important in studies on new classes of compounds.

The methods described above were employed to investigate the changes in the distribution of electron density on excitation and to determine μ_e and μ_g of a large number of compounds—in particular derivatives of naphthalene, stilbene, diphenyl, aniline, and pyridine[30-32,35,37], for the symmetrical molecules of which $\varphi = 0°$ or 180°. In this case, on excitation to the first singlet state, electron density shifts significantly along the conjugated bond chain from electron-donor to electron-acceptor substituents, this being accompanied by a marked increase of the dipole moment. A similar shift of electron density along the conjugated bond chain occurs also in symmetrically substituted phthalimides[30,37]. However, the greatest interest attaches to the application of these methods to molecules without a symmetry axis, for which $\varphi \neq 0°$ or 180°. Then, as already mentioned, it is possible to determine both the dipole moment μ_e and the angle φ and hence the direction in which electron density is displaced on excitation. The study of asymmetric derivatives of phthalimide[32,34,37] showed that, on excitation of these compounds, electron density is also markedly displaced from donor to acceptor functional groups, approximately along the line joining these groups (Fig. 2). In this connection, it is remarkable that the properties of the long-wavelength electronic transition responsible for the ability of phthalimides to fluoresce depend primarily on the properties of the substituents and the benzene ring appears to play a subsidiary role, behaving, as it were, as a conductor in charge transfer.

A study of $n-\pi^*$ and $n-\sigma$ transitions in molecules with a symmetry axis (acetone, nitromethane, methyl iodide, and bromoform) was undertaken by Bakhshiev[39] using a formula[31] suitable for molecules of this type:

$$\mu_e = \mu_g - \frac{C_1^a hca^3}{2\mu_g}\ , \quad (16)$$

where C_1^a is a constant determined from the shifts of absorption bands only in a series of solvents. The applicability of the method of universal interaction functions and in particular Eqns. (12) and (16) in the study of the physicochemical characteristics of certain molecular charge-transfer complex has been demonstrated[40]. The difference between the dipole moments of the first excited singlet and ground states of a number of benzene derivatives, calculated by the LCAO-MO method in the π-electron approximation and the same quantity determined experimentally by the method of universal interaction functions have been compared[41]. It has been shown that the theoretical and experimental results agree satisfactorily.

In the analysis of the electronic spectra of many organic compounds (in particular derivatives of phthalimide and stilbene), the long-wavelength bands of which correspond to intramolecular charge transfer, it has been found[37,42] that the difference between the dipole moments of the molecule in the ground and first excited electronic state $|\Delta\vec{\mu}|$, determined from the shifts in the spectra, is close in order of magnitude to the dipole moment of the transition $|\vec{D}|$, which is calculated from the intensity of the corresponding band. Since the comparison of $\Delta\vec{\mu}$ and $\vec{D}$ has a definite physical significance, the condition $|\Delta\vec{\mu}| \simeq |\vec{D}|$ can probably serve as one of the quantitative

criteria for the interpretation of the corresponding transition as an "intramolecular charge transfer" band (for further details, see also Saidov et al.[43]). This criterion was successfully employed by Kutsyna and coworkers for the assignment of bands in the spectra of 1,3,4-oxadiazole[44,45] and 1,3,5-triphenyl-2-pyrazoline[45] derivatives. In these and other investigations[45,47,48] Kutsyna and coworkers determined using Bakhshiev's method[29-35] the values of μ_e for the above compounds, the angle φ for 1,3,5-triphenylpyrazoline and its derivatives, and μ_e and μ_g for certain 1,3,4-oxadiazole derivatives, for which $\varphi = 0°$ or 180°. For the latter compounds, values of μ_g and μ_e in fairly good agreement with experimental data were calculated by the LCAO-MO method in the Hückel approximation.

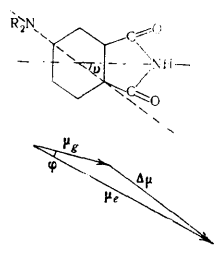

Figure 2. Orientation of the vector $\Delta\vec{\mu}$ relative to the molecular skeleton of 4-aminophthalimide (long-wavelength electronic transition).

The results of the determination of the dipole moments μ_g and μ_e by Bakhshiev's method[29-36] agree well in most cases with the results of other investigators, who employed both similar and completely different methods[31]. At the same time Bakhshiev's method[29-36] makes it possible to obtain relatively simply additional information about the excited state (the orientation of $\vec{\mu}_e$ and the anisotropy of the redistribution of electron density), which cannot be secured by the majority of similar procedures.

The method of determination of μ_e and φ from the shifts of the absorption and fluorescence bands was also proposed independently by Bilot and Kawski[49-56]. Like McRae and Ooshika, they solve[49] the quantum-mechanical problem of the interaction of the molecule with the solvent in second-order perturbation theory and then use the Onsager model. However, in contrast to the earlier investigators[4,5], Bilot and Kawski do not neglect the polarisibility of the molecule but take into account, as in Bakhshiev's work[29,57], the average polarisibility α, which is the same for the ground and excited states. In the special case where it is possible to neglect the polarisibility of the molecules ($\alpha = 0$), Eqn. (2), derived by Lippert and Mataga, follows from the formula of Bilot and Kawski. In the general case Bilot and Kawski[49], following Bakhshiev, assume that $\beta = 2\alpha/a^3 \simeq 1$ (a is the Onsager radius), which simplifies significantly the final relation. Then the formulae of Bilot and Kawski, relating the shifts of the absorption and fluorescence spectra to the parameters of the solvent and the test molecule, assume the following form[53]:

for absorption spectra:

$$\Delta\nu_a = -m_3\left(\frac{2n^2+1}{n^2+2}\right)\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right)-m_2\frac{3}{2}\frac{n^4-1}{(n^2+2)^2}, \quad (17)$$

for fluorescence spectra:

$$\Delta\nu_f = -m_4\left(\frac{2n^2+1}{n^2+2}\right)\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right)-m_2\frac{3}{2}\frac{n^4-1}{(n^2+2)^2}, \quad (18)$$

and for the Stokes shift:

$$\nu_a - \nu_f = m_1\frac{2n^2+1}{n^2+2}\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right)+\text{const.}, \quad (19)$$

where

$$m_1 = \frac{2(\vec{\mu}_e-\vec{\mu}_g)^2}{hca^3}, \quad m_2 = \frac{2(\mu_e^2-\mu_g^2)}{hca^3},$$
$$m_3 = \frac{2\vec{\mu}_g(\vec{\mu}_e-\vec{\mu}_g)}{hca^3}, \quad m_4 = \frac{2\vec{\mu}_e(\vec{\mu}_e-\vec{\mu}_g)}{hca^3}. \quad (20)$$

The following obvious relations obtain between the parameters m:

$$m_3 = \frac{m_2-m_1}{1}, \quad m_4 = \frac{m_1+m_2}{2}. \quad (21)$$

Using Eqns. (17)-(21), Bilot and Kawski[49-56] determined the dipole moments in the excited state μ_e and the angle φ between $\vec{\mu}_g$ and $\vec{\mu}_e$, with a and μ_g known. In order to calculate μ_e and φ, it is sufficient to find two independent parameters (out of four), for example m_1 and m_2, and then use the following working formulae:

$$\mu_e = \sqrt{\mu_g^2+\frac{1}{2}m_2hca^3}, \quad (22)$$

$$\cos\varphi = \frac{1}{2\mu_g\mu_e}\left[(\mu_e^2+\mu_g^2)-\frac{m_1}{m_2}(\mu_e^2-\mu_g^2)\right], \quad (23)$$

which are virtually the same as Eqns. (12) quoted above. The parameter m_1 is determined as in Bakhshiev's method[29-36] from the slope of the linear plot based on Eqn. (19). The remaining parameters, in particular m_2, can be found most simply from a graphical comparison of the theoretical and experimental shifts of the spectra of the solutions relative to the spectrum of the vapour or a solution in a non-polar solvent [for example on the basis of Eqn. (18)]. When $\varphi = 0°$ or 180°, we obtain from Eqns. (20) and (21)

$$\mu_g = \frac{m_2-m_1}{2}\sqrt{\frac{0.5\,hca^3}{m_1}},$$
$$\mu_e = \frac{m_2+m_1}{2}\sqrt{\frac{0.5\,hca^3}{m_1}}, \quad (24)$$

i.e., by analogy with Eqn. (15), an independent determination of the dipole moments in the ground and excited states is possible. The authors applied this method in the measurement of the dipole moments μ_e of derivatives of stilbene, fluorene, several phthalimides (for the majority of which $\varphi \neq 0$), naphthols, naphthylamines, and a number of other compounds. In particular, Bilot and Kawski[51,53] determined in addition to μ_e the angle φ for phthalimide derivatives, they subsequently measured μ_e for a number of other compounds[54] (including stilbene derivatives) with known values of μ_g and $\varphi \simeq 0$, and finally Kawski[56] determined from Eqns. (24) the values of μ_g and μ_e for naphthols.

On excitation of the molecules of all the compounds investigated to the first singlet state, the dipole moment increases. The experimental values of $|\Delta\vec{\mu}|$ for naphthols and naphthylamines[55] agree satisfactorily with the values calculated theoretically by Mataga and coworkers. The values of μ_e which they obtained agree also with the data of Bakhshiev, Czekalla, Meyer, and Wick (see below) but differ considerably (are lower than) from the analogous data of Lippert. According to these authors, this is

because Lippert fails to take into account the role of the polarisibility of the molecule in the ground and excited states.

In Abe's studies [58-61] a formula whereby it is possible to determine from the shift of the spectra both the dipole moment μ_e and the polarisibility of the molecule α_e in the excited state (using the results of the theoretical study of Margenau [62]) was derived from a direct consideration of the van der Waals interaction between the solvent and solute molecules with a large number of various simplifying assumptions (in particular the assumption that the molecules are spherical and that their polarisibility in combined electronic states is isotropic). To facilitate the calculations, the formula is written in the following simple form [59]:

$$(\mu_e^2 - \mu_g^2) + A\alpha_e = B \ , \qquad (25)$$

where A and B are quantities which depend in a complex manner on a number of the parameters of the test molecule and the medium and have different forms depending on the degree of interaction of the solvent molecules (the significance of the remaining quantities is clear from the foregoing). The method of determination of μ_e and α_e consists in plotting a linear relation between B and A for 7-10 solvents. It is then possible to find α_e from the slope, while the intercept on the ordinate axis yields $B = \mu_e^2 - \mu_g^2$, whence μ_e can be found provided that μ_g is known.

Abe and coworkers used this method to determine the values of μ_e and α_e in $^1B_{1u}$ and $^1B_{2u}$ excited states of the non-polar naphthalene molecule [59] and also in the $n-\pi^*$ excited state of the acetone molecule [60]. In the last case μ_e is much lower than the corresponding values for the ground state. It is also remarkable that the dipole moment μ_e which Abe obtained for acetone proved to be much less than the value which he calculated from the McRae formula (Robertson's method [24]). This last finding the author explains by the fact that McRae did not take into account the polarisibility of the molecule in the excited state, whereas according to Abe's data it increases markedly on excitation of the molecule. Somewhat earlier, while testing the relation which he derived Abe [58] determined, using a less rational method, the polarisibilities and dipole moments of nitrobenzene and acetophenone molecules in the excited state and then, using a simplified formula for the spectral shift, he found the values of μ_e and μ_g also from the spectral shift in non-polar solvents. He established thereby that electronic excitation increases the dipole moments of the molecules. Finally, using his method, Abe determined the dipole moments and polarisibilities in the excited states of four benzene derivatives (nitrobenzene, anisole, acetophenone, and *p*-chloroacetophenone). The high dipole moments of nitrobenzene and acetophenone (μ_e = 6.780 and 4.230 D respectively) were attributed to charge transfer on excitation.

An important feature of Abe's method [58-61] is that he does not employ the model concepts of the physics of dielectrics (in particular the Onsager model), i.e. there is no need to specify or determine independently the Onsager radius of the molecule. Unfortunately, however, the method [58-61] as a whole is based on not altogether correct postulates (the author does not take into account the Franck-Condon principle in the system "test molecule-medium" in the electronic transition and neglects the possibility that the moments $\vec{\mu}_g$ and $\vec{\mu}_e$ are not parallel, etc.), which probably makes this method suitable only for qualitative or semi-quantitative estimates. Furthermore, the applicability of the method is significantly complicated by the fact that it is necessary to know a number of physicochemical parameters of the test substance and the solvent which are difficult to determine.

In a number of studies an attempt was made to use certain of the above relations to determine the dipole moments of the excited state from the measured spectral shifts of the solutions as a function of temperature. The principal advantage of such methods consists in the fact that a smaller number of solvents is required to obtain the necessary data. The physical properties of the solvents and hence also the energy of the interaction of the test molecule with the medium, both in the ground and excited states vary with temperature, which leads to a shift of the electronic spectra. Piterskaya [63] determined μ_e and φ for a number of phthalimide derivatives with the aid of Bakhshiev's formulae (10)-(12). For this purpose, only five solvents (isopentyl alcohol, ethyl acetate, dioxan, anisole, and benzene) were required, instead of the usual 10-15. The dielectric constant ϵ and the refractive indices n of these solvents varied with temperature in the range 20-300°C ($\tau_{or} \ll \tau_{fl}$). The data obtained by this method agree well in most cases with the results obtained in the study of the spectral shifts as a function of the solvent at room temperature [32,34,37].

Pikulik and coworkers [64,65] attempted to extend the limits which restrict the applicability of the McRae formula to liquid solutions and derived a formula suitable for viscous and solid solutions:

$$\nu_{00}^a - \nu_{00}^f = \frac{2(\vec{\mu}_e - \vec{\mu}_g)}{hca^3}\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right)\frac{\tau_{fl}}{\tau_{fl}+\tau_{or}} \ . \qquad (26)$$

On the basis of this formula the authors proposed a method for the determination of the dipole moment $\vec{\mu}_e$ by analysing the mirror-image absorption and fluorescence spectra in one solvent (in particular in isobutyl alcohol) at low ($\tau_{or} \gg \tau_{fl}$) and room ($\tau_{or} \ll \tau_{fl}$) temperatures. In Eqn. (26) ν_{00}^a and ν_{00}^f are the frequencies of the purely electronic transitions for absorption and emission respectively. These frequencies may be determined by the method proposed by Pikulik for mirror-image spectra [66]. Eqn. (26) was used to determine $\vec{\mu}_e$ for several phthalimide derivatives with known $\vec{\mu}_g$ and φ (taken from Bakhshiev) and an Onsager radius $a \simeq 4$ Å. The data obtained in this study differ somewhat from Bakhshiev's results but, as pointed out by the authors, when certain additional factors are taken into account, the agreement becomes fairly satisfactory.

For fluorescent but sparingly soluble compounds, it is convenient to employ a method involving the approximate determination of the change in the dipole moments on excitation ($|\Delta\vec{\mu}| = |\vec{\mu}_e - \vec{\mu}_g|$) proposed by Löber [67]. This method involves the measurement of the positions of the fluorescence band maxima only at low ($\tau_{or} \gg \tau_{fl}$) and room ($\tau_{or} \ll \tau_{fl}$) temperatures in one solvent. The method is based on the Lippert-Mataga theory [see Eqn. (2)], and the final relation is of the form

$$(\nu_f)_T - (\nu_f)_t = \frac{2}{hca^3}\left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right)|\Delta\vec{\mu}|^2, \qquad (27)$$

where $(\nu_f)_T$ and $(\nu_f)_t$ are the frequencies at the fluorescence band maxima at low and room temperatures respectively. Löber suggests that the measurements may be performed in any solvent because the additional shift of the fluorescence bands due to possible specific interactions over short distances (in particular due to hydrogen bonding) is eliminated in Eqn. (27). Löber determined $|\Delta\vec{\mu}|$ for a series of aminoquinols with a merocyanine group on transition to the first excited singlet state. The solvent

was ethanol because its viscosity (and hence τ_{or}) varies gradually with temperature. In all cases the dipole moment of the molecules was found to increase on excitation and the properties of the substituents proved to be correlated with $|\Delta\bar{\mu}|$ (the Onsager radius a was assumed to be 3 Å). It was also established that, for compounds of the type investigated, non-radiative transitions from excited states with a large dipole moment have a high probability. Unfortunately the data obtained by Löber cannot be compared with the results of other workers.

Summarising, it must be noted that the methods for the experimental determination of μ_e and φ based on the measurements of spectral shifts, are fairly reliable and experimentally simple. It has been shown that these methods do not require the use of any special equipment and reduce solely to the measurement of the contours of the absorption and emission bands for solutions of the test substance in various solvents using standard spectroscopic apparatus. The accuracy of the spectral shift method is almost entirely determined by the accuracy with which μ_g and a are specified. In those cases where the values of a are specified on the basis of chemical structure, the error of the determination may reach 15–20%. However, it should be noted that at present studies are being carried out with the aim of developing methods for the direct experimental determination of a for substances which are not liquid at room temperature. Such methods can evidently significantly increase the precision of the determination of μ_e and φ.

III. METHOD OF ELECTRICAL POLARISATION OF FLUORESCENCE

In 1959 Czekalla [68-70] suggested that the phenomenon of the polarisation of the fluorescence of molecules in liquid solutions placed in an electric field (electrical polarisation of fluorescence) be used to determine the dipole moments of the excited states of the fluorescing molecules. The central feature of this phenomenon consists in the fact that, under the action of a strong electric field of about 150 kV cm^{-1}, the excited polar molecules of the solute are oriented and, on excitation with ultraviolet light, emit partially polarised fluorescence, the degree of polarisation P being low: $P = \dfrac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$, where $I_{\parallel}$ and $I_{\perp}$ are the intensities of the fluorescence polarised parallel and perpendicular to the direction of the electric field respectively. According to the classical phenomenological theory developed by Czekalla, the degree of polarisation of the fluorescence P varies linearly with the square of the field strength:

$$P_E - P_0 = 0.1\,\frac{3\cos^2\alpha - 1}{2}\left(\frac{\mu_e}{kT}\right)^2\left(\frac{\varepsilon+2}{3}\right)^2 E^2, \qquad (28)$$

where P_E is the degree of polarisation of the fluorescence of the solution in a field E for a solvent with a dielectric constant ϵ, P_0 the degree of polarisation for the same solution without the field, the α the angle between the vector of the electronic transition moment and the dipole moment of the excited state $\vec{\mu}_e$. This angle can be determined either by measuring the electrical dichroism (see below) or on the basis of additional considerations concerning the molecular structure [70]. In the derivation of Eqn. (28) it is assumed, firstly, that the same excited state is responsible for both absorption and fluorescence and, secondly, that the ratio of the average lifetime of the excited state (τ_F) to the dielectric relaxation (principally orientation) time of the molecules in solution (τ_ϵ) is sufficiently large for the attainment of orientation equilibrium in the excited state ($\tau_F/\tau_\epsilon > 3$). The ratio τ_E/τ_ϵ can be determined, for example, from measurements of the degree of polarisation of the fluorescence of the solution P_0 without an electric field using the formula

$$\frac{\tau_F}{\tau_\varepsilon} = \frac{P_\infty - P_0}{P_0(3 - P_\infty)}, \qquad (29)$$

where P_∞ represents the degree of polarisation of the fluorescence for a solvent with infinite viscosity (usually $P_\infty \simeq 0.45$).

In Czealla's phenomenonological theory only factors associated with the anisotropy of the distribution of the polar molecules oriented by the external electric field are considered but no account is taken of the shift of the fluorescence band occurring because the different dipole moments in the ground and excited states interact in different ways with the external field. Nevertheless, analysis shows that this last factor can have decisive importance in many cases. Therefore Liptay [71] developed a quantum-mechanical theory of the effect of electric fields on the fluorescence of solutions and derived formulae for different experimental conditions giving the relation between the degree of polarisation of fluorescence, on the one hand, and the strength of the external electric field and the form of the fluorescence band, on the other. In these formulae, which were obtained for particular values of the ratio τ_F/τ_ϵ, account is taken of the shift of the fluorescence band on application of the electric field. In its general form this relation is very complex, so that the experimental determination of the dipole moments of excited states using such formulae is possible only in special cases.

In the study of the polarisation of fluorescence by an external field, both linearly polarised and non-polarised ultraviolet radiation can be used for excitation, fluorescence perpendicular to the direction of the distribution of the exciting radiation being observed in both cases. Although the working formula is simpler than in the first case, nevertheless it is desirable to employ non-polarised radiation, because the intensity of the fluorescence and hence the precision of the experiments is thereby considerably increased. With this method of excitation, the following relation, derived with certain simplifying assumptions (in particular assuming the conditions $\vec{\mu}_g \parallel \vec{\mu}_e$), is used to determine μ_e:

$$\frac{P_{E\nu} - P_{0\nu}}{E^2\left(\frac{\varepsilon+2}{3}\right)^2}\left(1 + \frac{0.9}{\tau_F/\tau_\varepsilon}\right) = 0.1\,\frac{\mu_e^2}{k^2T^2} + 0.2\,\frac{\mu_e(\mu_e - \mu_g)}{hckT}\,\frac{d\ln I_\nu}{d\nu}, \qquad (30)$$

where I_ν is the intensity of fluorescence with frequency ν and the significance of the remaining quantities is the same as in Eqn. (28). The first term of Eqn. (30) describes orientation effects and the second is due to the displacement of the band under the influence of the field E. The ratio τ_F/τ_ϵ is related by means of Eqn. (31) to the degree of polarisation of fluorescence in the absence of the field when excited by non-polarised radiation:

$$P_0 = \frac{0.3}{0.9 + \tau_F/\tau_\varepsilon}. \qquad (31)$$

For liquid solutions, $\tau_F/\tau_\epsilon \gg 1$ and Eqn. (30) becomes simpler:

$$\frac{P_{E\nu} - P_{0\nu}}{E^2\left(\frac{\varepsilon+2}{3}\right)^2} = 0.1\,\frac{\mu_e^2}{k^2T^2} + 0.2\,\frac{\mu_e(\mu_e - \mu_g)}{hckT}\,\frac{d\ln I_\nu}{d\nu}. \qquad (32)$$

This expression can be used for both excitation methods mentioned above[71].

If the conditions $\tau_F/\tau_\epsilon \gg 1$ does not hold, Eqn. (30) is used to estimate μ_e to a first approximation and the estimate is then employed to calculate μ_e to a second approximation by the above general formula containing terms which depend on the form not only of the emission but also of the absorption bands. This procedure greatly complicates the calculation of μ_e but it is necessary in all cases where $\tau_F/\tau_\epsilon \leqslant 1$.

In the determination of the moments μ_e by the method of electrical polarisation of fluorescence, the left-hand side of Eqn. (30) is plotted against $d\ln I/d\nu$. It is significant that the values of μ_e can then be found by two independent methods†: from the intercept which the straight line makes on the ordinate axis and from the slope of the straight line (for known μ_g). Czekalla et al.[72] state that the first method is more accurate and gives rise to an error not exceeding 5%. It is striking that the two methods yield closely similar results in most cases.

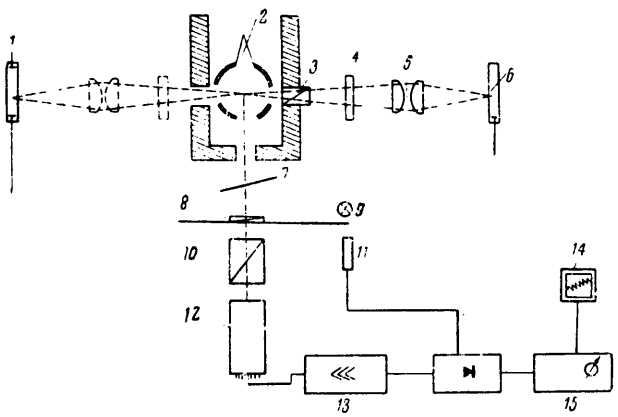

Figure 3. Outline of the apparatus for the determination of $\Delta\bar{\mu}_e$ by electrical polarisation of fluorescence: 1) NVO-200 mercury lamp; 2) cuvette; 3) polariser; 4) filter; 5) condenser; 6) NVO-200 mercury lamp; 7) compensator; 8) $\lambda/2$ plate; 9) reference signal lamp; 10) analyser; 11) photo-cell; 12) photomultiplier; 13) amplifier; 14) pen recorder; 15) valve voltmeter.

The apparatus employed by Czekalla and coworkers for the measurement of the degree of polarisation of fluorescence in an electric field is shown schematically in Fig. 3. The excitation of fluorescence is achieved by radiation from one or two high-pressure mercury lamps. The exciting radiation passes through a light filter which isolates intense lines from the mercury arc spectrum and the light is focussed by means of condensers on the specimen placed between the electrodes of the measuring high-voltage chamber. The radiation from the right-hand side lamp can be linearly polarised by means of a polariser built into a calibrated rotating ring. The measuring high-voltage cuvette is fitted with electrodes of special form (Rogovskii's profile) to exclude edge effects. A constant high potential chosen to give $E \simeq 150$ kV cm^{-1} is applied to the electrodes, the distance between which is 0.465 cm.

The system is thermostatted by passing a special liquid with a high resistivity and a high breakdown voltage through the hollow electrodes. The chamber is fitted with a special device in the form of a bent matt-black tube designed to eliminate the effect of scattered light.

Partially polarised fluorescence is observed in the direction perpendicular to the exciting beam. The beam analysed passes through a half-wave plate rotating at a definite frequency, and then through a rigidly fixed analyser. By means of this device, the polarised part of fluorescence is modulated at a definite frequency and a variable signal is transmitted to a photoelectric multiplier (PEM), is amplified, rectified, and fed to an electronic voltmeter coupled to a pen recorder. The non-polarised part of luminescence remains non-modulated and is therefore not recorded. The signal from the polarised component of the fluorescence can be concentrated by rotating the plane of the compensator through a definite angle. From this angle, read off a dial, it is possible to calculate the degree of polarisation of the fluorescence, using Fresnel's formulae[68]. The auxiliary signal from the incandescent lamp is modulated at the same frequency as the polarised light and controls the operation of the rectifier, locking it to the rotation of the plate.

To determine the degree of polarisation as a function of frequency within the limits of the fluorescence band, it is necessary to place a monochromator or an interference filter between the analyser and the photoelectric multiplier[71,72]. Particular attention is paid to the preparation of the specimen. Apart from the usual methods of purification, it is necessary to degas the solution carefully in order to avoid the electrical breakdown of the specimen in the powerful electric field.

The method of electrical polarisation of fluorescence was used to determine the dipole moments of the excited states of a number of derivatives of a biphenyl, fluorene, and stilbene in benzene and dioxan and also the complex of tetrachlorophthalic anhydride with hexamethylbenzene[70]. Comparison of the results obtained by the method of electrical polarisation of fluorescence with those determined from spectral shifts and by the method of electrical dichroism (see below) shows that the agreement is satisfactory in all the cases investigated.

IV. METHOD OF ELECTRICAL DICHROISM

The phenomenon of electrical dichroism was observed and explained for the first time by Kuhn et al.[73] It consists in the fact that a solution placed in a powerful electric field exhibits anisotropy of absorption in the region of the electronic bands of solute molecules. Hence it follows that, after passage through the solution, natural light becomes partially polarised (degree of polarisation P_E) and the intensity of initially linearly polarised light depends on the angle between the directions of light polarisation and the electric field.

Electrical dichroism is explained by partial orientation of solute molecules in the powerful electric field in consequence of their permanent dipole moment or the anisotropy of their polarisability. It is significant that, under the action of the electric field, the absorption band is also displaced in proportion to the difference $\mu_g - \mu_e$ because of the difference between the dipole moments and polarisibilities of the molecule in the ground and excited states.

†The same also applies to Eqn. (32).

A theory of the phenomenon, taking into account the band shift and therefore making it possible to relate P_E to μ_e, was developed by Liptay and Czekalla [74,75] and also by Labhart [76] (for polarisable molecules). Several versions of this method for the determination of the dipole moments of excited states, differing in the method of measurement of electrical dichroism, were proposed by Liptay, Czekalla, and Wick [69,75,77] and by Labhart [78,79].

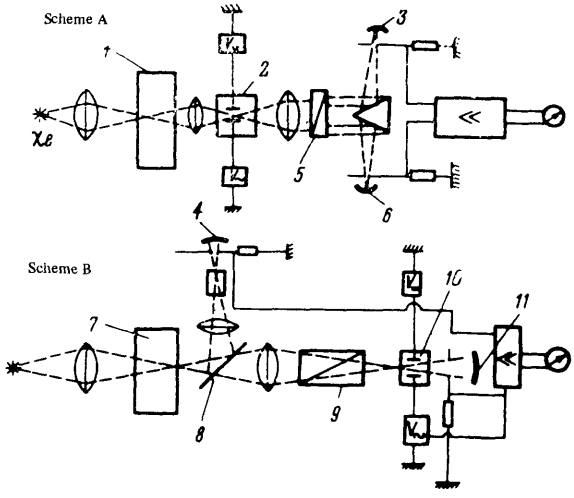

Figure 4. Outline of the apparatus for the determination of $\vec{\mu}_e$ by the method of electrical dichroism: 1) monochromator; 2) cuvette; 3) photomultiplier; 4) photomultiplier; 5) analyser; 6) photomultiplier; 7) monochromator; 8) half-silvered plate; 9) Nicol prism; 10) measuring cell; 11) photomultiplier.

In Czekalla's method‡ (Fig. 4, scheme *A*) the degree of polarisation of natural light at frequency ν is investigated in an electric field of 20–90 kV cm^{-1} (ν is in the region of the absorption band of the solution). Light from a xenon lamp is directed through a monochromator into a measuring cuvette, placed in a steady electric field interrupted at a frequency of 75 Hz. After passing through the analyser, the partially polarised light falls upon the photocathode of the photoelectric multiplier, the signal from which is amplified and recorded.

For the simplest case, in which the dipole moments $\vec{\mu}_g$ and $\vec{\mu}_e$ and also the dipole moment of the electronic transition $\vec{M}$ are parallel, the following relation is valid:

$$P_{E_\nu} = -2.3 D_\nu \left(0.1 \frac{\mu_g^2}{k^2T^2} + 0.46 \frac{(\mu_e - \mu_g)\mu_g}{hckT} \frac{d \lg \varepsilon_\nu}{d\nu}\right)\left(\frac{\varepsilon+2}{3}\right)^2 E^2, \quad (33)$$

where P_{E_ν} is the degree of polarisation of light at a frequency ν which has passed, in a direction perpendicular to that of the field E, through a solution with an optical density $D\nu$, molar extinction coefficient ϵ_ν, and dielectric constant ϵ. It is readily seen that the number μ_e can be found from the slope of the linear plot of P_E against E^2 knowing the value of μ_g and having determined experimentally D_ν and $d \lg \epsilon_\nu / d\nu$. In the more complex case the method permits the determination also of the angle between the vectors $\vec{\mu}_g$ and $\vec{\mu}_e$ and the dipole moment of the transition $\vec{M}$.

In the method for the investigation of electrical dichroism proposed by Labhart, measurements were made of the intensity of light at frequency ν polarised at a definite angle relative to the direction of the field and transmitted through the absorbing solution at right angles to the direction of the field (Fig. 4 scheme *B*). In this case the light leaving the monochromator falls on a half-silvered mirror which divides the beam into two components: one passes through the comparison cuvette (without an electric field) and the other is polarised and passes through the measuring cuvette to which a constant high potential interrupted at a frequency of 75 Hz has been applied. Both beams are received by the photomultiplier cells and the signals are amplified and transmitted to the apparatus in which the difference between them is recorded.

In Labhart's method the relative change in the intensity of the polarised light I which has passed through the solution without a field (through the comparison cuvette) and in the presence of the field E is also linearly related to E^2 and in the simplest case ($\vec{\mu}_e \parallel \vec{\mu}_g$) the corresponding formula is

$$\frac{\Delta I}{I} \equiv q_E = -\frac{5.29}{3} D_\nu \frac{(\mu_e - \mu_g)\mu_g}{hckT} \frac{d \lg \varepsilon_\nu}{d\nu} \left(\frac{\varepsilon+2}{3}\right)^2 E^2. \quad (34)$$

It is readily seen that the dipole moment μ_e can also be obtained from Eqn. (34) given μ_g and having calculated $d \lg \epsilon_\nu / d\nu$ from the absorption spectrum.

Using a method of measurement analogous to that described above [79] and the theory of optical absorption by molecules in solution in an electric field which they developed previously [80,81], Liptay and coworkers determined the dipole moments in the ground and excited states and also the dipole moments of the electronic transitions of a number of symmetrical molecules (nitrobenzene, 4-nitroaniline, 3,5-diamino-1-nitrobenzene, 3,5-dinitroaniline, carbazole, and 3,6-dinitrocarbazole) in dioxan [82]. The results agree well with the determinations of μ_g by the usual electrical methods and also with simple theoretical calculations of μ_g and μ_e. Comparison of the experimental and theoretical data makes it possible to assign to charge transfer two absorption bands of 3,6-dinitrocarbazole. The combination of the methods of measurement proposed by Czekalla and Labhart provides a convenient method for the determination not only of dipole moments but also (in more complex cases) of the mutual orientations of the vectors of the dipole moments and the transition moments. The available methods for the observation of electrical dichroism and also the electrical polarisation of fluorescence have been reviewed in detail [78,79]. The dipole moments μ_e of a number of derivatives of stilbene, fluorene, and biphenyl have also been determined by the method of electrical dichroism. In most cases the results were compared with data obtained by other methods and satisfactory agreement was found.

V. METHOD BASED ON THE STARK EFFECT

The method of determination of the dipole moments of molecules in the ground state from the splitting of the rotational lines in an electric field (Stark effect) measured by microwave spectroscopy is well known [83]. In order to

‡The method of measurement by Czekalla's method described here is due to Labhart [78,79]. For Czekalla's scheme, see, for example, Ref. 69.

use the Stark effect for the determination of the dipole moments of the excited states of molecules, it is necessary to observe the splitting of the fine rotational structure of the vibronic bands in the absorption spectra in an electric field, i.e. optical spectroscopic methods must be used. Such splitting becomes observable in the fairly strong electric fields employed to investigate the electronic spectra of gaseous diatomic or simple monotomic molecules whose rotational structure is well resolved. This of course greatly restricts the choice of the possible objects for investigation.

The dipole moments of $n-\pi^*$-excited states of simple organic molecules (formaldehyde and propynal) were determined for the first time by Freeman and Klemperer [84-86] and the corresponding dipole moment of formyl fluoride was determined by Lombardi et al. [87] Even for these comparatively simple organic molecules, it is not possible to observe complete splitting of the rotational structure. However, when the mutually perpendicular polarised Stark components in the formaldehyde spectrum are observed separately, well resolved doublets are revealed. This makes it possible to determine the dipole moment of the excited state after identifying the bands, provided that the dipole moment of the ground state, the splitting between the components of the doublet, and the electric field strength are known. A different procedure is used for the propynal molecule: after calculating the Stark spectra for postulated dipole moments and comparing them with those observed experimentally, the authors choose the most suitable value of the dipole moment.

It should be noted that only for molecules of the symmetric top type (the formaldehyde molecule may be regarded as such) is it possible to determine by this method the overall dipole moment μ_{ea} of the molecule along the axis of rotation directed along the bond C=O. In other cases it is necessary to determine also the component of the dipole moment μ_{eb} in the plane perpendicular to the direction of μ_{ea}. Despite its restricted applicability, the method based on the Stark effect is important, since it makes it possible, using a simple model, to observe the change in the dipole moment on excitation of the molecule in the gaseous phase, by the most direct method.

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It is useful to compare briefly the characteristics of modern methods used to determine the dipole moments of excited states. As can be seen from the foregoing, the methods most widely used at present are based on the measurement of spectral shifts under the influence of the solvent. These methods are distinguished by simplicity of experimental technique and of the formulae used for the calculations. The preferred methods [29-38,49-56] are those which permit the determination not only of the magnitude but also of the orientation of the moment $\vec{\mu}_e$ relative to $\vec{\mu}_g$, allowing at the same time the role of the polarisability (particularly for molecules with not very large permanent dipole moments). It has been shown [8-16] that failure to take into account the polarisability leads to significantly high values of $\vec{\mu}_e$. However, methods based on the measurements of spectral shifts constitute at the same time also the most approximate procedures for the determination of the permanent dipole moments of free molecules. This is due to the approximations made in the derivation and in the practical application of the formulae required for the calculation. This includes the obligatory use of the simple Onsager model of the interaction between the solute molecule and the solvent and also the necessity to specify or determine independently the Onsager radius which enters into the formulae of the majority of methods based on spectral shifts§. Moreover, another disadvantage of these methods is the need to employ a large number (10-15) of solvents with specially selected values of ϵ and n in order to obtain a sufficiently reliable result; this limits their applicability to sparingly soluble compounds. From this point of view, methods based on the measurements of the temperature variation of the spectral shift, in which the number of solvents required for the investigation is greatly reduced, are very promising.

Unfortunately the most convenient versions of the method of spectral shifts are applicable only to fluorescent molecules and permit the determination of $\vec{\mu}_e$ for the first singlet excited state only. Therefore, despite their approximate nature, the methods based on the analysis of the displacement of absorption spectra alone also merit attention, since they permit the determination of the dipole moments of the higher excited and non-fluorescent (for example $n-\pi^*$) states [18,19,27,39].

The formulae for the determination of $\vec{\mu}_e$ by electrical polarisation of fluorescence were derived on a more rigorous basis. At the same time, for the practical application of these formulae it becomes necessary to make additional simplifying assumptions (for example no account is taken of terms containing polarisibility) which introduce significant systematic errors into the results. Furthermore, there are experimental difficulties associated with the fact that, due to the very weak polarisation of luminescence under the action of an external electric field, a very powerful electric field must be employed, which may lead to the breakdown of the experimental cuvette. This risk leads in turn to the necessity for preliminary careful treatment (degassing) of the solution (usually in benzene). However, even in very powerful fields the effect remains small, which necessitates the employment of very sensitive methods for the recording of the polarised luminescence. This greatly complicates the apparatus and excludes the possibility of the determination of $\vec{\mu}_e$ of weakly luminescent compounds. Because of these considerations, the method of polarised fluorescence is less attractive, although it remains nevertheless the only fairly accurate method for the determination of $\vec{\mu}_e$ in the fluorescent (equilibrium) excited state of the molecule in non-polar solvents.

The method of electrical dichroism permits the determination of the dipole moment of an excited non-equilibrium (Franck-Condon) state with a relatively high precision, although in this case the final formulae are appreciably simplified by various (sometimes very approximate) assumptions. The experimental technique, which remains very complex, is nevertheless simpler than in the previous method because in this case a weaker field is required and the intensity of the partially polarised emission recorded is relatively high. Furthermore, the method is more general, since it permits the determination of μ_e of both fluorescent and non-fluorescent molecules and also of higher excited non-fluorescent singlet and triplet states. Finally, the procedure used to calculate $\vec{\mu}_e$ is much simpler than in the method of polarised fluorescence. All these factors undoubtedly constitute

§Here attention should be drawn to Eqns. (15) and (25) and also the method employed by Baba [22] in which the Onsager radius need not be known for the determination of μ_e.

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definite advantages of the method of electrical dichroism and it is desirable that it be widely employed by the determination of $\vec{\mu}_e$.

The Stark effect has a restricted applicability, as already mentioned. However, this is the most accurate and

Experimental dipole moments of organic compounds in excited electronic states.

№	Compound	μ_g, D	μ_e, D	Method	Refs.
	I. Aromatic compounds				
1	Nitrobenzene	4.0—4.2	6.78	S	61
			9±2	D	82
2	Acetophenone	3.0—3.8	4.23	S	61
			$n\pi^*$0.5	S	18
3	Aniline	1.6	$\Delta\mu$ 2—2.5	S	17
			6.0	S	27
4	4-Nitroaniline	6.2	14	D	77
			15.5	D	82
5	Anisole	1.35	2.37	S	61
6	*p*-Chloroacetophenone	2.23	2.68	S	61
7	3,5-Diamino-1-nitrobenzene	5.8	$1B_2$ 11.8	D	82
			$2A_1$ 15.7	D	82
8	2,5-Dinitroaniline	6.1	11.8	D	82
9	*p*-Dimethylaminobenzonitrile	6.55	23	S	11
			15.7(0°)	S	54
			14.9	F_1	72
			11.1	F_2	72
10	*NN*-Dimethyl-4-nitrosoaniline	6.7—6.9	11.7	S	38
			11.5	D	77
11	*NN*-Dimethyl-4-nitroaniline	6.85	15.0	D	
12	*p*-Nitroanisole	4.8	6.89	S	19
13	4-Dimethylamino-ω-nitrostyrene	7.7	18.0	F_1	72
			17.8	F_2	72
			18.0	D	7
14	Azulene		^1L_b —0.81	S	24
			^1L_a —0.32	S	24
			^1B_b +1.0	S	24
15	Naphthalene	0	0	S	59
16	α-Naphthylamine		$\Delta\mu$ 4.4	S	15
			$\Delta\mu$ 4.1	S	55
17	β-Naphthylamine		$\Delta\mu$ 3.5	S	15
			$\Delta\mu$ 3.4	S	55
18	α-Naphthol	1.5	$\Delta\mu$ 0.5—1.0	S	13
		(1.4)	2.5	S	36
			2.67	S	56
19	β-Naphthol	1.5	$\Delta\mu$ 0.5—1.0	S	13
		(1.8)	3.6	S	36
			3.28	S	56
20	Methyl β-naphthyl ether	1.2	$\Delta\mu$ 0.5	S	12
		(1.2)	2.9	S	36
			2.8	S	56
21	Hexamethylbenzene-tetrachlorophthalic anhydride complex	3.6	14±3	S	70
			7.6(50°)	S	52
			10±1.5	F_1	70
22	4-Amino-4′-nitrobiphenyl	6.0	18	S	10
		(6.7)	16.3(0°)	S	36
			14.5(0°)	S	54
			22.8	F_1	72
			22.2	F_2	72
			23.0	D	77
23	4-Dimethylamino-4′-nitrobiphenyl	6.6	21.2	F_1	72
			23.1	F_2	72
			24.0	D	77
24	4-Amino-4′-cyanobiphenyl	6.0	13.0	F_1	72
			15.3	F_2	72
			16.5	D	72
25	2-Amino-7-nitrofluorene	5.8	25	S	10
		(6.6)	19.7(0°)	S	36
			17.3(0°)	S	54
			18.6	F_1	72
			19.2	F_2	72
			23.0	D	77
26	4-Amino-4′-nitrostilbene	6.5	23.5	F_1	72
			23.4	F_2	72
			22.0	D	77
27	4-Dimethylamino-4′-nitrostilbene	7.1	32	S	10
		(7.3)	24.8(0°)	S	36
			24.7(0°)	S	54
			25.1	F_1	72
			25.2	F_2	72
			26.5	D	77
28	4-Methoxy-4′-nitrostilbene	(5.3)	19.3(0°)	S	36
29	4-Cyano-4′-dimethylaminostilbene	7.1	29	S	10
			$\Delta\mu$ 14	S	36
			21.5(0°)	S	54
			20.2	F_1	72
			21.2	F_2	72
			20.0	D	77
30	4-Dimethylaminobenzylidene-4′-nitroaniline	8.6	38	S	10
		(7.9)	26.2(0°)	S	36
			26.5(0°)	S	49
	II. Heterocyclic compounds				
1	Pyrazine	0	0	S	22
2	Pyridazine	3.94	$n\pi^*$1.10	S	22
3	Pyrimidine	2.2	$n\pi^*$—0.52	S	22
4	Carbazole	1.6—1.9	$\Delta\mu$ 2.2	S	14
			3.1±0.7	D	82
5	Acridine	(9.0)	11.5(0°)	S	31
6	2,5-Diphenyloxadiazole	(3.5)	6.0	S	4
7	2-(4-*N*-Dimethylaminophenyl)-5-phenyl-1-oxa-3,4-diazole	5.13	16.05(0°)	S	44
8	2,5-Diphenyloxazole	1.55	5.1(0°)	S	44
9	2,5-Di-(*p*-anisyl)-1-oxa-3,4-diazole	4.2	8.0(0°)	S	47
10	4-Aminophthalimide	3.5	7.1(15°)	S	36
			7.1(20°)	S	63
			6.8(16°)	S	53
11	3-Aminophthalimide	2.6	5.2(20°)	S	36
			5.1(20°)	S	63
			4.9(19°)	S	51
12	3-Monomethylaminophthalimide	2.7	5.7(25°)	S	36
			5.5(35°)	S	63
13	3-Dimethylaminophthalimide	2.7	5.6(25°)	S	36
14	3-Acetamidophthalimide	2.4	4.1(65°)	S	36
			4.5(90°)	S	51
15	3,6-Diaminophthalimide	2.14	4.7(0°)	S	36
		(2.3)	4.5(0°)	S	63
			5.4(0°)	S	51
16	6-Amino-3-dimethylaminophthalimide	2.14	4.6(40°)	S	32
			4.8(33°)	S	51
17	3,6-Bis(dimethylamino)phthalimide	(2.2)	5.7(0°)	S	36
18	3,6-Diacetamidophthalimide	(5.5)	0(0°)	S	36
19	4-Amino-*N*-methylphthalimide	3.6	9.9	S	64
20	*N*-methyl-4-monomethylaminophthalimide	3.7	10.3	S	64
21	*N*-Methyl-4-dimethylaminophthalimide	3.7	11.15	S	64
22	4-Acetamido-*N*-methylphthalimide	4.6	9.8	S	64
23	3-Amino-*N*-methylphthalimide	2.7	7.2	S	64
24	3-Acetamido-*N*-methylphthalimide	2.4	5.1	S	64
25	γ-[4-5-Hydroxy-3-phenyliso-oxazolyl)-4-butadienyl]-*N*-methylpyridinium betaine	(29)	19	S	36
26	Phenol Blue	5.8	7.5—9.1	S	5
			⩾10.2	S	28
27	Aminoquinols with a merocyanine group		$\Delta\mu$ 3.5—5.5	S	67
28	Dimethylnaphtheurhodine	2.0	12	S	8
29	3,6-Dinitrocarbazole	6.6	19.0	D	82
30	1,3,5-Triphenylpyrazoline	2.58	7.7(40°)	S	46
31	3-(*p*-Chlorophenyl)-1,5-diphenyl-2-pyrazoline	3.39	10.8(23°)	S	46
32	1-(*p*-Chlorophenyl)-3,5-diphenyl-2-pyrazoline	3.87	10.0(40°)	S	46
33	9,10-Diazaphenanthrene	3.93	$n\pi^*$1.15	S	23
	III. Aliphatic compounds				
1	Methyl iodide	1.5	$n\sigma^*$—0.7	S	39
2	Nitromethane	3.2	$n\pi^*$2.9	S	39
3	Bromoform	1.0	$n\sigma^*$—1.7	S	39
4	Formaldehyde	2.34	$n\pi^*$ 1.56	St	85
5	Formyl fluoride	0.595	$n\pi^*$ 1.65	St	87
6	Acetone	2.7—2.8	$n\pi^*$ 1.4	S	39
			$n\pi^*$ 0.86	S	60
7	Propynal	2.39	$n\pi^*$ 0.7	St	86
8	Mesityl oxide		7.6	S	28
9	Thiourea	4.9	$n\pi^*$ 2.5	S	21
10	*N*-Methylthiourea	4.2	$n\pi^*$ 0.1	S	21
11	*NN′*-Diethylthiourea	4.9	$n\pi^*$ 2.8	S	21
12	Tetramethylthiourea	4.7	$n\pi^*$ 0.1	S	21

NOTES TO TABLE

1. In a few cases the limiting values employed by various authors to determine μ_e are indicated in the μ_g column and the figures in brackets represent values obtained by the spectral shift method.

2. In the μ_e column the figures in brackets represent the angles between $\vec{\mu}_g$ and $\vec{\mu}_e$ proposed on the basis of structural considerations when these are 0° or 180°, or obtained by the spectral shift method if they are not 0° or 180°; the values of $|\Delta\vec{\mu}|$ (and not $|\vec{\mu}_e|$) obtained from spectral shifts and also μ_e for the $n-\pi^*$ and $n-\sigma^*$ states and states the symmetry of which is known are indicated on the left-hand side by the appropriate symbols. All the remaining values refer to the lowest singlet excited electronic states.

3. The significance of the symbols in the "method" column is as follows: S—spectral shift method; F_1 and F_2—method of electrical polarisation of fluorescence in which the values of μ_e are determined from the slope or from the intercept on the ordinate axis respectively; D—method of electrical dichroism; St—method based on the Stark effect.

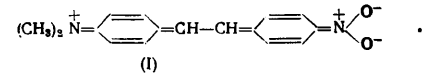
4. All the values of μ_e obtained by the F_1, F_2, and D methods are given for solutions in benzene with the exception of compounds 9 and 29 in Class I whose values are quoted for solutions in dioxan.

direct method for the determination of the dipole moments of excited states of free (i.e. unperturbed by the solvent) molecule. Furthermore, it appears that there is hope that the application of more refined analytical methods and better apparatus will extend somewhat the range of objects susceptible to investigation by this procedure.

It follows from the foregoing that various methods, despite their disadvantages, supplement one another to a considerable degree, which makes it desirable to determine $\vec{\mu}_e$ simultaneously by several of the above methods in important cases.

In conclusion a Table is presented in which the results of the determination of the dipole moments of the excited states of many molecules and complexes by different investigators using the methods described above are compiled. These data lead, in the first place, to the important conclusion that the values of $\vec{\mu}_e$ obtained by different procedures are similar. This finding shows that both the postulates on which the methods employed are based and the results themselves are correct. Furthermore, the data permit certain interesting conclusions to be drawn concerning the electronic structure of the excited states of organic molecules.

Thus comparison of $\vec{\mu}_e$ and $\vec{\mu}_g$ indicates a considerable increase of the polarity of many molecules in the excited state compared with the ground state. For example, in 4-dimethylamino-4′-nitrostilbene this indicates a considerable contribution of the dipolar structure (I) to the electronic state attained when the molecule is excited in the region of the long-wavelength electronic system:

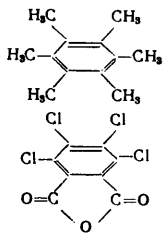


(I)

As already mentioned, the increase of polarity on electronic excitation of the molecule is in general characteristic of many singlet excited states of substances with active functional groups. This behaviour is shown particularly clearly for stilbene, fluorene, and biphenyl derivatives investigated by all the available methods and also oxadiazole and triphenylpyrazoline derivatives. On excitation, not only the magnitude but also the direction of the dipole moment usually changes appreciably. The direction of the vector for the difference between the dipole moment in the excited and ground states indicates the migration of charge from a donor to an acceptor group (transitions with charge transfer). These results, obtained mainly in the study of phthalimides [30,32,34,37,51,53], were described in detail above. Here we shall mention only that they agree well with the conclusions of many theoretical investigations [1,44,45,88].

Interesting data were obtained in the study of the dipole moments of the excited $\pi-\pi^*$ state of alternant and non-alternant hydrocarbons. It was found [59], in particular, that the naphthalene molecule is non-polar in the $^1B_{1u}$ and $^1\Gamma_{2u}$ excited states, as in the ground state, in agreement with the postulates of the molecular orbital theory. The azulene molecule remains polar also in $\pi-\pi^*$ excited states [24], but the direction of $\vec{\mu}_e$ in the first two singlet excited states is the opposite of that of $\vec{\mu}_g$. This indicates electron transfer from the five-membered to the seven-membered ring on excitation. The measurements of $\vec{\mu}_e$ of the first singlet excited state of certain molecular charge-transfer complexes yielded decisive proof of a sharp increase in the polarity of the complex in the excited state. Furthermore, it has been shown, for example [40,57], that in the formation of the iodine complex of 4-methoxycarbonylpyridine there is complete electron transfer from the aromatic molecule to the iodine atom with formation of an ion pair.

The dipole moment $\vec{\mu}_e$ of the sandwich type complex (II), determined by Lippert's spectral shift method and by the method of electrically polarised fluorescence, amounts to 14 ± 3.0 D and 10 ± 1.5 D respectively [70], which indicates an appreciable charge transfer from hexamethylbenzene to tetrachlorophthalic anhydride on excitation (the calculated moment of the structure D^+A^- is about 16 D, while $\vec{\mu}_g$ is only 3.6 D).



(II)

If however, one does not begin with the assumption that the vectors of the difference between the dipole moments of the steady states and the dipole moment of the electronic transition are parallel, as was done by Czekalla and Meyer [70], and the angle between the moments $\vec{\mu}_e$ and $\vec{\mu}_g$ is determined by the spectral shift method, then, as shown by Bilot and Kawski [52], the angle is about 50° and, although the polarisation in the excited state does increase, the increase is much less than found in the preceding investigation ($|\vec{\mu}_e| = 7.6$ D). These results are confirmed by those of Bakhshiev [40].

On transition of molecules to the $n-\pi^*$ excited state, the polarity of the molecule diminishes appreciably compared with the ground state in the majority of cases. Thus the values of $\vec{\mu}_e$ determined by the Stark method for the $n-\pi^*$ states of formaldehyde and propynal are much lower than the corresponding values of $\vec{\mu}_g$. Analogous relations between $\vec{\mu}_e$ and $\vec{\mu}_g$ on $n-\pi^*$ excitation are characteristic also of other carbonyl compounds (various ketones [18] and acetones [39,60]). This is evidence that the transition to the $n-\pi^*$ excited state is localised at the carbonyl group and is associated with its polarisation in the direction opposite to that which obtains in the ground state. The results of recent measurements of $\vec{\mu}_e$ of nitromethane [9,10,39] diazaphenanthrene [23], and derivatives of thiourea [21], pyridazine, and pyrimidine [22] lead to similar conclusions, that is, the decrease of the dipole moment on $n-\pi^*$ excitation, and, for pyrimidine, the reverse direction of the vector $\vec{\mu}_e$ with respect to that of the vector $\vec{\mu}_g$. Similar changes in the direction of the dipole moment on excitation are particularly characteristic of the $n-\sigma^*$ transition [39] (methyl iodide, bromoform), which is evidence of a more important displacement of electron density on $n-\sigma^*$ excitation compared with the $n-\pi^*$ transition. The results of Lombardi et al. [87] do not agree, however, with the concept of the localisation of excitation at a C=O group in the $n-\pi^*$ excitation of the formyl fluoride molecule, since the dipole moment would not then decrease and its sign would remain the same.

The above data for the difference between the changes of dipole moments in charge-transfer $\pi-\pi^*$ and $n-\pi^*$ transitions lead to the conclusion that the difference is one of the principal factors which determine the direction of the shift of the corresponding absorption band when non-polar solvents are replaced by polar solvents (the so called red and blue spectral shifts). The latter, in turn, throws light on the nature of solvatochromism, linking it

mainly to the difference between the electrostatic interactions of the molecules with the solvent in the ground and excited states in consequence of the change in the dipole moment of the molecule in the quantum jump.

Despite the large number of published studies, the investigation of the dipole moments of excited states has essentially only just begun. The main importance of the results obtained consists in the fact that the dipole moment of the excited state is at the present time virtually the only experimental quantity characterising its electronic configuration.

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Leningrad State University
Rostov-on-Don State
University

U.D.C. 541.64

Semirigid Chain Molecules

V.N.Tsvetkov

The problem of the extent to which the hydrodynamic and optical behaviour of chain molecules in solutions can be used for the observation and the quantitative assessment of their rigidity and of the internal ordering of their structures is examined. The general theoretical positions are illustrated by experimental results for a series of polymers, the molecules of which have a rigid chain structure. There is a bibliography of 106 references.

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I. INTRODUCTION

A characteristic property of chain molecules of polymers is their flexibility, that is, their ability to change conformation under the influence of thermal motion or under the action of deforming forces. This property explains the rubberlike behaviour of high-molecular-weight elastomers in the temperature range above their glass points. In solutions such flexible chain molecules have the conformation of a statistical coil which in Θ conditions (an "ideal" solvent) can be regarded as a "gaussian" coil.

The properties of solutions of flexible chain molecules have been the subject of detailed and thorough study by many investigators and have been described in several reviews and monographs [1-10].

In connection with the development of the synthesis of polymers suitable for the creation of high-strength and thermally stable fibres, films, and other materials for special purposes, the need for a study of the morphological and conformational properties of the macromolecules of such polymers has become increasingly evident in recent years.

The chemical structure of these macromolecules shows that many of them, despite their chain structure, should have limited flexibility, occupying a position intermediate between the absolutely rigid submicroscopic species (such as viruses or globular proteins) and the ideally flexible chain molecules of many synthetic polymers.

The classical examples of such "semirigid" chain molecules are the molecules of natural celluloses, and also of polypeptides and nucleic acids in helical conformation. Until comparatively recently our practical information about rigid chain molecules was limited to these examples. However, in recent years various investigators synthesised new polymers, the macromolecules of which show the properties characteristic of semirigid chain molecules.

II. THEORETICAL PRINCIPLES

1. Conformation and Rigidity of the Molecular Chain

The estimation of the rigidity or flexibility of a macromolecule can be approached in various ways, leading to two concepts: thermodynamic (equilibrium) and kinetic (non-equilibrium) flexibility. The opinion about the equilibrium flexibility of the chain is divided on the basis of a study of the equilibrium conformation (dimensions and geometric form) which the macromolecule adopts in various media.

Information about kinetic flexibility has been obtained by investigating the rate of occurrence of the processes which convert the macromolecule from one conformation into another.

Although there are grounds for assuming that for a definite molecular structure both types of flexibility are interconnected, the extent and nature of this relation in each individual instance requires special study.

The first of the two above-mentioned types of flexibility—equilibrium flexibility (and the corresponding rigidity) of chain molecules will be examined below. A quantitative measure of the equilibrium rigidity of a molecular chain could be the length of a statistical segment A (Kuhn and coworkers [10]) or the persistent length of the chain $a = A/2$ (Porod [11]).

The length A is determined from two conditions [10]. The first is the equality $L = NA$, where N is the number of segments in the chain and L its contour length, that is, the length of the chain at its greatest extension without destroying the valence angles and bonds; when an ordered secondary structure is present in the molecules (for example, the α-helix type) the retention of this structure during the extension must be borne in mind. The second condition is formulated as follows: at long chain lengths ($L \gg A$) and in the absence of higher order interactions [12] it is modelled by a gaussian chain, that is, the mean square distance between its ends $\overline{h^2}$ is proportional to its contour length $\overline{h^2} = NA^2$. The combination of these two conditions leads to the equation

$$A = \overline{h^2}/L \qquad (1)$$

valid for a gaussian chain.

When the contour length L is insufficient for satisfying the conditions $L \gg A$, $N \gg 1$ (which for rigid chain molecules, where A is large, can occur at rather high values of L, that is, in the range of rather large molecular weights), then the molecular chain is not gaussian and relation (1) is not satisfied.

In this instance an effective method of describing the conformational properties of a molecule is the model of a "persistent" or "wormlike" chain [11]—a three-dimensional line of constant curvature. This curvature is characterised by the parameter a—the persistent length (correlation length) [11-15]; a is determined by the relation

$$a = -\Delta L / \ln \overline{\cos \Delta\theta},$$

where $\Delta\theta$ is the angle between the tangents to the segment of the wormlike chain at its initial and final points. The bar denotes an average over all the conformations of the

chain corresponding to the given values of L and h. Hence a is a measure of the equilibrium rigidity of the chain, increasing with decrease in the convolution of the latter.

For persistent chains instead of formula (1) the theory[11,16] leads to the relations:

$$\overline{h^2}/L = A[1-(1/x)(1-e^{-x})], \quad (2)$$

$$6\overline{R^2}/L = A\{1-(3/x)[1-(2/x)\{1-(1/x)(1-e^{-x})\}]\}, \quad (3)$$

where $\overline{R^2}$ is the radius of gyration of the molecules, $x = L/a = 2L/A$. Equations (2) and (3) are applicable in any range of values of parameter x, that is, to chain molecules of any length under the condition of no effects of long-range order interactions (action at a distance).

In the limit, when $x \to 0$, from Eqns. (2) and (3) it follows that $h = L$ and $\overline{R^2} = L^2/12$, that is, the conformation of the molecule is similar to a linear bar. On the other hand, when x is large Eqns. (2) and (3) correspond to the properties of gaussian chains—Eqn. (2) is equivalent to Eqn. (1), and (3) gives $\overline{R^2} = \overline{h^2}/6$.

The variation of $\overline{h^2}/LA$ and $6\overline{R^2}/LA$ with x according to Eqns. (2) and (3) is shown by curves *1* and *2* in Fig. 1.

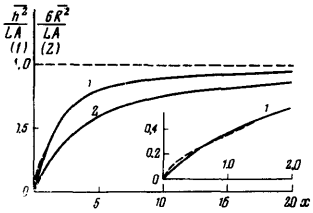


Figure 1. Variation of the statistical dimensions of a persistent (wormlike) chain with its contour length L. *1*) $\overline{h^2}/AL$ as a function of the parameter $x = L/A$. Continuous curve: according to theory[11]; broken curve: according to theory[17]. *2*) $6\overline{R^2}/AL$ as a function of $x = L/A$ according to theory[16].

For comparison with experimental results it is convenient to make the substitution $L = P\lambda$ in Eqns. (2) and (3) where P is the degree of polymerisation and λ the projection of the monomeric unit on the direction of the molecular chain. Instead of Eqn. (2) we obtain:

$$\overline{h^2}/P = S\lambda^2[1-(S/2P)(1-e^{-2P/S})] \quad (2')$$

where S is the number of monomeric units in the segment.

On plotting the experimental values of $\overline{h^2}/P$ as a function of P, a curve like curve *1* in Fig. 1 is obtained. Its initial slope gives λ^2, whereas the asymptotic level $S\lambda^2$ allows S to be determined and correspondingly $A = S\lambda$. The value of S can also be determined from the form of the curve, by its departure from the asymptotic limit at a given value of P (this departure is determined by the value of the parameter S/P). Similar results can be obtained from the experimental dependence of $6\overline{R^2}/P$ on P.

The advantage of the above wormlike model is its universality, since in it the flexibility of the molecular chain is determined without any a priori hypotheses about the mechanism of this flexibility (restricted or free rotation around the valence bonds, rotational isomerism defects of the secondary structure, etc.). On the other hand, starting from the experimental data on the dimensions of the molecules ($\overline{h^2}$ or $\overline{R^2}$) and the degree of their polymerisation P this theory not only allows the rigidity of the molecular chain to be estimated but also makes possible judgements about its conformation since the projection of the monomer λ is also determined in this.

On the other hand it can be shown that, for example, for a molecular chain with restricted rotation the persistent model leads to the same results as the calculation of $\overline{h^2}$ by the method of statistical mechanics in the rotational isomer approximation. Flory[18] recently developed such a method for application to chains of any length and used it for calculating the molecular dimensions of certain polymers[17,19]. The results are given as a plot of $\overline{h^2}/nl^2$ against n ($1 < n < \infty$), where n is the number of valence bonds in the chain with a valence angle of $\pi - \theta$ between neighbouring bonds, and l the length of the chain. This can be easily converted into the relation $\overline{h^2}/AL = f(x)$ on taking into account that in this instance

$$x = 2n\cos^2\frac{\vartheta}{2}/\lim_{n\to\infty}(\overline{h^2}/nl^2), \qquad A = l\lim_{n\to\infty}(\overline{h^2}/nl^2)/\cos\vartheta/2$$

and

$$L = nl\cos\vartheta/2.$$

The curve $\overline{h^2}/Al = f(x)$ for the polyethylene chain (from Flory and Jernigan's results[17]) is shown in Fig. 1 (broken curve). In the range $0.5 < x < \infty$ it coincides with curve *1* determined by Eqn. (2). The difference in the models is noticeable only for extremely short chains for which $x < 0.5$ and $n < 3$, that is, in the range of molecular weights without practical significance.

It should be borne in mind that all the relations examined, (1)–(3), characterising the skeleton rigidity of the chain (short-range action), assume the absence of effects of long-range action in the molecule and therefore strictly speaking are applicable only to chain molecules, which are found in a Θ-solvent.

In thermodynamically good solvents owing to the effects of the excluded volume (action at a distance) the dimensions of the molecular coils are increased and the molecular chains are no longer gaussian[12]. In the range of molecular weights where under Θ conditions relation (1) is obeyed, in good solvents it is not satisfied and can be replaced[1] by Eqn. (4):

$$\overline{h^2} = N^{1+\varepsilon}\cdot A^2 = A^{1-\varepsilon}L^{1+\varepsilon} \quad (4)$$

where $0 < \epsilon < 0.2$ and ϵ does not depend on L.[12]

Kurata and coworkers[20] concluded that in very good solvents the parameter ϵ can reach the value 1/3. From Eqn. (4), the effect of the excluded volume leads to an increase in $\overline{h^2}/L$ with increase in L, that is, it brings about a departure from gaussian properties of the same nature as the short-range action (rigidity of the chain) describable by Eqns. (1)–(3). However, the departure from gaussian properties due to the rigidity of the chain appears in the range of low molecular weights and disappears at higher molecular weights. On the other hand these departures due to action at a distance increase steadily with the molecular weight and therefore will appear in the range of high molecular weights. This circumstance allows (at least in principle) the effects of short-range and long-range action to be distinguished from the form of the dependence of $\overline{h^2}/L$ on L.

The effects of long-range action (non-ideality of the solutions) show the decisive influence on the conformation of flexible chain molecules and were considered in detail for such molecules in several monographs[1,4-8,12]. On the other hand, for rigid-chain polymers the excluded volume

effect, even in good solvents, is expressed relatively weakly and in several instances it cannot be taken into consideration.

In accordance with Eqns. (2) and (3) the study of the conformational properties and rigidity of the persistent chains requires the experimental determination of their molecular weights (degrees of polymerisation P) and radius of gyration $\overline{R^2}$. The first characteristic is readily determined by one of the well-known methods [1].

The determination of $\overline{R^2}$ is a much more complex task. A direct method which can be employed for this is the study of the angular asymmetry of light scattering by the polymer in solution [1]. However, it must be remembered that these measurements are usually accompanied by considerable experimental errors, since they must be made in the range of comparatively low molecular weights (where departure from gaussian properties occurs), in which the degree of asymmetry of light scattering is slight and is easily quenched by the presence of a minute amount of dust, the formation of molecular associates, or traces of the non-dissolved polymer, and also by other accidental factors. Therefore although there have been investigations (chiefly with cellulose derivatives) in which the dimensions and rigidity of the molecules were determined by the asummetry of light scattering method using the theoretical relations (2) and (3), their results are not always reliable and sometimes difficult to explain [21-23].

Another method of determining the rigidity of a molecular chain is the direct measurement of its persistent length $a = A/2$ using small-angle scattering of X-rays [24]. This method has as yet had only limited value since as well as the complexity of the experimental technique it is applicable only to polymers the scattering ability of which differs markedly from that for the pure solvent. In this connection it is the rule that in studying the conformation of molecules in solutions hydrodynamic methods are more widely employed.

2. Hydrodynamic Properties of Chain Molecules

The rigidity of a molecular chain is usually judged from its hydrodynamic properties in solutions by examining the variation of the sedimentation coefficient $[S]$, diffusion coefficient D, and characteristic viscosity $[\eta]$ with the molecular weight M.

This relation can be most simply represented in the form of Mark–Kuhn empirical expressions (M–K):

$$[\eta] = K_\eta \cdot M^\alpha, \tag{5}$$

$$D = K_D \cdot M^{-\beta}, \tag{6}$$

$$[S] = K_s \cdot M^{1-\beta}. \tag{7}$$

In measurements under Θ-conditions, that is, in the absence of the excluded volume effect, high values of α and β show the appreciable influence of the flowability effect, that is, the "loose" structure of the molecular coil and therefore can serve as an index of the increased rigidity of the molecular chain.

However, in non-ideal solvents the volume effects lead to osmotic distention of the coil and to a corresponding increase in the indices α and β, that is, they act in the same direction, as increased rigidity of the chain. Therefore to find the true ("skeleton") rigidity of the molecular chain the influence of the volume effects should be excluded.

For flexible chain polymers, the molecules of which are coiled in rather compact tangles even in good solvents, the hydrodynamic interaction inside the tangle is great and the flow effect is almost absent. For such molecules the influence of the volume effects can be excluded by extrapolation of the hydrodynamic properties to the range of low molecular weights using the effects of the excluded volume [12,25]. Eqn. (8) can be applied to the viscosimetric results for this purpose [26]:

$$[\eta]/M^{1/2} = (LA/M)^{1/2} \cdot \Phi + 0.51\,\Phi \cdot B \cdot M^{1/2}. \tag{8}$$

When using sedimentation or diffusion results, Eqn. (9) [27] or (10) [28] can be employed:

$$(DM^{1/2})^{-1} \equiv (1-\bar{v}\rho)\,M^{1/2}/[S]\,RT = (\eta_0 P_0/kT)\,[(LA/M)^{1/2} + 0.2\,BM^{1/2}], \tag{9}$$

$$(DM^{1/2})^{-3} = (\eta_0 P_0/kT)^3\,[(LA/M)^{1/2} + 0.51\,BM^{1/2}]. \tag{10}$$

Here $\Phi = 2.8 \times 10^{23}$, $P_0 = 5.11$, B is the parameter of the thermodynamic polymer–solvent interaction, η_0 the solvent viscosity, and L the contour length of the molecule.

On plotting the left part of Eqns. (8), (9), or (10) as a function of $M^{\frac{1}{2}}$, the intercept on the ordinate axis of the curve yields the undisturbed dimensions of the molecular chain and the corresponding rigidity, determined by the quantity A. However, this method is inapplicable for rigid-chain polymers, since for them the flow effect usually (although not always) plays a significant part.

Fortunately, for rigid chain molecules the excluded volume effect does not play a significant part, even in thermodynamically good solvents and can be neglected in the first approximation. Under such conditions the theory of the hydrodynamic properties of wormlike chains developed by Kuhn [29] and by Hearst and Stockmayer [30] (K-S) can be used for estimating the rigidity of the chain. At sufficiently high molecular weights when the molecule can be modelled by a gaussian chain, the K-S theory leads to the expressions

$$M/[\eta] = \Phi^{-1}\{(M/LA)^{1/2} M^{1/2} + 0.93\,[\ln(A/d) - 1.43]\,(M/L)^2 A^{-1}\}, \tag{11}$$

$$DM/RT = (1.843/3\pi\eta_0 N_A)\,(M/LA)^{1/2} M^{1/2} + (3\pi\eta_0 N_A)^{-1}\,(M/L)\,[\ln(A/d) - 1.43]. \tag{12}$$

Apart from the quantities L and A, which characterise the conformation and rigidity of the chain, Eqns. (11) and (12) contain the diameter d of the wormlike model, which must be allowed for in the correct description of its hydrodynamic properties.

On plotting the left part of Eqns. (11) or (12) as a function of $M^{\frac{1}{2}}$, the value of M/LA can be found from the slope of the straight line obtained, that is, the chain rigidity can be estimated. A/d and consequently the chain diameter d can be found from the intercept on the ordinate axis.

Eqns. (11) and (12) show that in the range of extremely large molecular weights when the first term on the right-hand side (dependent on M) is much greater than the second, the variation of the viscosity and diffusion coefficients with molecular weight is described by Eqns. (5)–(7) with indices $\alpha = \beta = 0.5$. Besides it must be borne in mind that in non-ideal solvents an increase in M is accompanied by an increase in the part played by the excluded volume effects; this leads to values of α and β exceeding 0.5. This effect is evidently observed in solutions of high-molecular-weight desoxyribonucleic acid [31,32].

At moderate values of M and considerable rigidity of the chain the part played by the second term on the right-hand side of Eqns. (11) and (12) becomes appreciable and there is a corresponding increase in the index α in Eqn. (5) to values approaching unity (cellulose derivatives, DNA).

Finally, for extremely rigid chain molecules in the range of low molecular weights, when the chain length $L \leq A$, but

much greater than the diameter d (slightly curved fine rods), theory[30] leads to the expression:

$$[\eta] = 2\pi N_A L^3 [45\,(M/L)\,(\ln\,(L/d) - 1.03)]^{-1} \cdot [1 - f\,(L/A)] \qquad (13)$$

from which it follows that the index in Eqn. (5) lies between 1 and 2. This is actually realised, for example, for polypeptide molecules in helical conformation[33]. Hence high values of the exponent in Eqn. (5) were obtained for these well-known rigid chain polymers.

However, this is by no means a general rule, since for gaussian chains the values of α and β are determined by the intramolecular hydrodynamic interaction, which depends on the diameter d as well as the degree of convolution L/A of the chain.

Thus from Eqns. (11) and (12) if the diameter of the molecular chain is d and is comparable with the length of the segment A—for example, $A \simeq 4d$ and $\ln(A/d) = 1.43$—then the indices α and β in Eqns. (5)–(7) will be close to 0.5, irrespective of the rigidity of the chain. A similar situation occurs, for example, for oligomers with flexible chain molecules[34-37]. As will be shown below, it can also occur with some rigid chain polymers where the segment length A is considerable (graft polymers)[38].

From what has been said above, the viscosity and translational friction for chain molecules and their dependence on the molecular weight can vary considerably. They are determined by the main parameters of the chain—diameter, contour length, and segment length, and also depend on the thermodynamic interaction of the molecules with the solvent. Consequently in several instances use of hydrodynamic properties alone seems insufficient for the quantitative determination of the rigidity, conformation, and internal structure of macromolecules.

The information obtainable becomes much more complete when a study of the hydrodynamic properties of the solutions is supplemented by an investigation of their dynamo-optical and electro-optical properties.

3. Dynamo-optical Properties of Chain Molecules[39]

The segment length A or the persistence length $a = A/2$, being a measure of the equilibrium rigidity of the main chain of the molecules, reflects to a certain extent another important property, the orientation order in the molecule. However, optical anisotropy is a more direct and much more sensitive measure of the orientation ordering of the structure of the molecule.

The optical anisotropy of a chain molecule of a polymer is measured by the difference between two of its principal polarisabilities $\gamma_1 - \gamma_2$ in directions parallel to and perpendicular to the vector h joining the ends of the chain.

For the simplest model—a gaussian chain[29]—the optical anisotropy of the molecule in the equilibrium conformation is independent of its contour length, that is, the molecular weight, and close to the anisotropy of the segment $\alpha_1 - \alpha_2$:

$$\gamma_1 - \gamma_2 = \frac{3}{5}(\alpha_1 - \alpha_2) \qquad (14)$$

The difference in polarisability of the segment $\alpha_1 - \alpha_2$ depends on the anisotropy of a monomeric unit $a_\parallel - a_\perp$ and the number of monomeric units S constituting the segment:

$$\alpha_1 - \alpha_2 = S\,(a_\parallel - a_\perp)\ . \qquad (15)$$

Therefore molecules with high rigidity (that is, having a high value of S) are characterised by high optical anisotropy.

On the other hand it has been shown that the swelling of molecules in good solvents, which greatly alters their dimensions and hydrodynamic properties, has hardly any effect on their optical anisotropy[1,39,40]. Therefore anisotropy can serve as a measure of the true skeletal rigidity of the molecular chain, irrespective of the effects of excluded volume, that is, the thermodynamic interaction of the molecule with the solvent.

It is very important that the anisotropy of the monomeric unit $\alpha_\parallel - \alpha_\perp$, and also the anisotropy of the molecule, can be either positive or negative, depending on the degree and nature of the ordering of the valence bonds of the monomeric unit relative to the direction of the main chain. Therefore optical anisotropy is a measure of the axial orientation order in the arrangement of the structural elements of the molecule—both of the main chain and also its lateral groups.

In a system having a uniaxial orientation order the degree of this order Q is known[41] to be given by:

$$Q = \frac{1}{2}(3\overline{\cos^2\theta} - 1) \qquad (16)$$

where θ is the angle of the departure of the longitudinal axis of the structural element (segment) from the direction of preferential orientation (that is, from the direction of the vector h in the molecule). $\overline{\cos^2\theta}$ is a quantity obtained by averaging over all the orientations of the segments in the molecule, at given values of $\bar{h}^2$ and L.

From Eqns. (15) and (16) there is a simple relation between the degree of orientation order Q and the anisotropy of the molecule:

$$Q = (\gamma_1 - \gamma_2)/P\,(a_\parallel - a_\perp) \qquad (17)$$

where P is the degree of polymerisation.

Experimentally, the anisotropy of the molecule described by a gaussian chain can be determined by measuring the double refraction Δn in flow in solution of the polymer being studied and a calculation by Kuhn's formula[10]:

$$\Delta n/\Delta\tau = \Delta n/g\,(\eta - \eta_0) = [n]/[\eta] = [4\pi\,(n_S^2+2)^2/45kTn_s](\alpha_1 - \alpha_2). \qquad (18)$$

Here $\Delta\tau = g(\eta - \eta_0)$ is the effective shear stress in flow with a velocity gradient of g, $[n]$ is the characteristic birefringence of the solution, with $[n] = (\Delta n/g\eta_0 c)_{c \to 0}$ where c is the concentration.

When the refractive index of a polymer n_k differs from that of a solvent n_S, an additional positive anisotropy of the molecule arises, owing to the optical interaction of parts of the chain with one another—the "form effect"[39,42].

The overall form effect can be divided into two parts—the "macroform" effect and the "microform" effect. The first of these is due to the interaction of parts rather far apart along the chain (optically long-range action) and is determined by the asymmetry of the form of the macromolecular coil as a whole. The double refraction of the macroform for a gaussian chain equals:

$$([n]/[\eta])_f = [0.058\,\Phi\,(n_s^2+2)^2(n_k^2 - n_s^2)^2/\pi\rho^2 N_A RTn_s^3](M/[\eta]) \qquad (19)$$

where Φ is the Flory coefficient, and ρ the density of the polymer. For a given polymer–solvent system the macroform effect is proportional to $M/[\eta]$ and therefore increases with the molecular weight.

The "microform" effect is due to the optical interaction of parts of the molecule which are neighbours along the chain. Unlike the macroform effect, the double refraction of the microform for a gaussian chain is independent of the molecular weight but proportional to the molecular weight

of a segment $M_S = A(M/L)$ and consequently increases with the rigidity of the chain:

$$([n]/[\eta])_{fs} = [(n_s^2+2)^2 (n_k^2 - n_s^2)^2/180\pi RTn_s^2\rho](L_2 - L_1)_s \cdot M_s \quad (20)$$

where $(L_2 - L_1)$ is the coefficient of the asymmetry of the form of the segment.

The principal role in the total, experimentally observable form effect for flexible chain molecules is taken by the macroform anisotropy, Eqn. (19), whereas for molecules with high skeletal rigidity of the chain it is the macroform anisotropy, Eqn. (20). Therefore for rigid-chain molecules the experimental measurement of the microform effect is an independent method of determining the skeletal rigidity of the molecular chain.

A characteristic feature of the macroform effect is its marked decrease with increase in the concentration of the solution[1,43]. On the other hand, the quoted value of the microform birefringence $[\Delta n/g(\eta - \eta_0)]_{fs}$ varies little with concentration[39,42]. Therefore a study of the concentration dependence of the form birefringence can enable the relative parts of its macro- and micro-constituents to be estimated and information obtained about the rigidity of the polymer investigated.

If the contour length L of a chain molecule is not very great in comparison with the segment length A (that is, the condition $h \ll L$ is not satisfied), it can no longer be regarded as a gaussian chain and Kuhn's formula (14) is inapplicable.

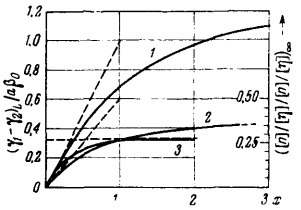


Figure 2. Variation of the optical anisotropy of the persistent length $(\gamma_1 - \gamma_2)_L$ and reduced birefringence of the solution $[n]/[\eta]$ with the parameter $x = L/a$. *1*) $(\gamma_1 - \gamma_2)_L/a\beta_0$ as a function of x; *2*) $\cdot[n]/[\eta]_L/[n]/([\eta])_{x\to\infty}$ as a function of x; *3*) $(\gamma_\parallel - \gamma_\perp)_L/a\beta_0$ as a function of x.

In this instance the difference in the principal polarisabilities $(\gamma_1 - \gamma_2)_L$ of molecules of length L is calculated by the theory of persistent anisotropy[44], which yields the relation

$$(\gamma_1 - \gamma_2)_L = \frac{3}{5}(\alpha_1 - \alpha_2)(1 - e^{-6x/6}) = a\beta_0 x\left[1 - \frac{5}{12}x + \frac{25}{216}x^2 - \frac{125}{5184}x^3 + \ldots\right], \quad (21)$$

where $x = L/a$, $a = A/2$, and $\beta_0 = (\alpha_1 - \alpha_2)/A$ is the anisotropy of unit length of the chain.

In distinction from the gaussian chains the anisotropy of a persistent chain increases with its length L (and consequently, the molecular weight), tending (at $x \to \infty$) to a limiting value of $\frac{3}{5}(\alpha_1 - \alpha_2)$ corresponding to the anisotropy of a gaussian chain. The corresponding dependence is shown in curve *1*, Fig. 2, where the ratio $(\gamma_1 - \gamma_2)_L/a\beta_0$ is represented as a function of the parameter x. The initial slope of the curve is evidently 1, the limiting value equals 6/5.

On plotting the values of $(\gamma_1 - \gamma_2)_L$ as a function of the contour length L of the molecule, then according to Eqn. (21), the initial slope of the curve determines the value of β_0, whereas the asymptotic limit gives a value of $\frac{6}{5}a\beta_0$.

It must be remembered that according to theory—Eqn. (21)—the decrease in molecular anisotropy with chain shortening is determined solely by the parameter $x = L/a$, and not by the absolute length of the segment A. Consequently, this phenomenon should occur not only for rigid but also for flexible chain molecules in the range of rather low molecular weights (oligomers). In reality the decrease in flow anisotropy with decrease in molecular weight was observed experimentally in oligomers with flexible chain molecules[37] although their hydrodynamic behaviour exhibited no special features.

This phenomenon is of special significance for rigid-chain molecules (large A) since then it should be observed in the range of rather high molecular weights and can serve as a direct proof of increased skeletal rigidity of the chain.

In accordance with Eqn. (21) and unlike the gaussian coils, Eqn. (18), the flow birefringence $([n]/[\eta])_L$ in solution of persistent chains should increase with the molecular weight, tending to a limiting value of $([n]/[\eta])_\infty$ as $x \to \infty$, determinable by Eqn. (18).

For rigid wormlike chains ($A \gg d$) in the range of low x ($x < 3$) this increase is determined by the formula:

$$([n]/[\eta])_L = (4\pi/45\,kTn_s)(\gamma_1 - \gamma_2)_L \cdot F(x) \cdot (n_s^2+2)^2, \quad (22)$$

where $F(x)$ is a tabulated[44] function reflecting the change in the geometric asymmetry of the molecules with increase in length, and the value of $(\gamma_1 - \gamma_2)_L$ is determined by Eqn. (21).

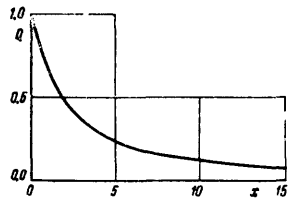


Figure 3. Variation of the degree of intramolecular orientation ordering Q with the parameter $x = L/a$ for a persistent chain.

The variation of $([n]/[\eta])_L/([n]/[\eta])_\infty$ with x, according to Eqn. (22), is represented by curve *2* of Fig. 2. The initial slope of the curve obtained is 0.5, the asymptotic limit is 1.

A comparison of the experimental dependence of the birefringence on the molecular weight with the theoretical (22) enables the anisotropy of unit length β_0 and the persistence length $a = A/2$ of the molecular chain to be determined.

Eqn. (21) also enables the change in the degree of intramolecular orientation order Q with increase in chain length to be presented clearly. On combining Eqns. (21), (17), and (14) and taking into account that $P/S = x/2$, we obtain:

$$Q = (6/5x)(1 - e^{-6x/6}). \quad (23)$$

Fig. 3 shows the dependence of Q on x according to Eqn. (23). With increase in x the degree of ordering falls sharply from values close to unity to values close to zero.

Values of $Q \simeq 1$ are characteristic of systems with an almost perfectly ordered structure, which occurs, for example, in ideal three-dimensional single crystals.

Less perfect, but nevertheless extremely high, orientation order is observed in liquid crystalline (mesomorphic) systems; thus for a nematic mesophase the value of Q lies in the range 0.4–0.7.[41]

As the graph in Fig. 3 shows, the same level of orientation ordering in the structure of chain molecules can be achieved in the range of molecular weights where x does not exceed a few units. Several examples can now be given (see below) of extremely rigid chain molecules for which this range corresponds to molecular weights of tens and even hundreds of thousands.

For such "crystal-like" polymeric molecules the degree of intramolecular orientation order corresponds to the level of the supermolecular organisation of the nematic mesophase.

However, for most flexible-chain polymers even at $P \simeq 10^3$, Q has an order of magnitude of 0.01 and this decreases with a further increase in molecular weight. Such a low degree of orientation order can be observed and measured only by using such sensitive quantities as the optical anisotropy of the molecule determinable from the stream birefringence.

These features of the optical properties of rigid-chain molecules, predicted by theory, are independent of both excluded volume effects and of hydrodynamic interaction in the molecular chains. Therefore the use of these properties as characteristics of rigidity and the degree of ordering of the structure of a molecule is not complicated by a need to allow for the thermodynamic quality of the solvent and a flow effect.

4. Electro-optical Properties

In examining the order of the structure of macromolecules a distinction must be made between orientation axial order and orientation dipole order. Many chain molecules contain polar groups or bonds and in the presence of a coaxial order in the mutual orientations of these groups the macromolecule should have a high total dipole moment. However, for flexible chain molecules this is usually not observed. One of the reasons can be the mutual compensation of the local and group moments in their vector addition. The main reason is the flexibility of the macromolecule, which results in local polar groups of the molecule in an external electric field being orientated practically independently of one another. Here the dipole polarisation of the molecule in an electric field is simply equal to the sum of the polarisation of its polar units and does not differ much from the polarisation of a liquid monomer of equal mass.

For rigid-chain molecules the situation can be significantly different. Owing to the rigidity of the molecular structure the orientations of the polar groups of the molecule in an electric field are independent of one another but are mutually correlated to a greater or less extent with the molecular chain or its parts (segments). Therefore if the vector sum of the local group moments is not equal to zero, that is, if their orientation-polar ordering inside the molecule is realised, the latter can have a significant dipole moment and under the action of an electric field it rotates as a rigid particle.

Note that these properties of the molecule depend not only on its equilibrium rigidity but also to a considerable extent on its kinetic rigidity.

In solutions of such polar rigid-chain molecules a high birefringence is produced in an electric field E (the Kerr effect). The value of Δn and the sign of the birefringence depend on the magnitude and sign of the optical anisotropy of the molecule $\gamma_1 - \gamma_2$ and also on its dipole moment μ and the angle θ formed by the axis of the dipole with the optical axis of the molecule[45]:

$$\lim_{\substack{c\to 0\\ E\to 0}} (\Delta n/cE^2) = \frac{\pi N_a}{15n}\left(\frac{n^2+2}{3}\right)^2\left(\frac{\varepsilon+2}{3}\right)^2 \cdot \frac{\gamma_1-\gamma_2}{M}\left(\frac{\mu}{kT}\right)^2 (3\cos^2\vartheta - 1). \quad (24)$$

Here c is the concentration, n the refractive index, and ϵ the dielectric constant of the solution.

An experimental study of this effect and a comparison of the results with those on flow birefringence enables information to be obtained about the value and direction of the molecular dipole and additional conclusions to be drawn about the conformation, rigidity, and ordering of the structure of the molecule.

On modelling a semirigid molecule by a persistent chain the value of its dipole moment μ can be linked[11,46] with the contour length $L = ax$ by the theoretical relation:

$$\overline{\mu^2} = (\mu_0 S)^2 (x - 1 + e^{-x})/2 \quad (25)$$

or

$$\overline{\mu^2}/L = (\mu_s^2/A)[1 - (1 - e^{-x})/x], \quad (26)$$

where μ_0 is the component of the dipole moment of the monomeric unit along the axis of the molecule, S the number of monomeric units in its segment, and μ_S the dipole moment of the segment.

An experimental study of the variation of the dipole moment μ with the molecular weight M and a comparison of this relation with the theoretical one—Eqns. (25) and (26)—enables the persistent length a to be found and hence the rigidity of the molecule to be estimated from electro-optical results.

In a periodic electric field solutions of rigid-chain polar molecules exhibit a dependence of the Kerr effect on frequency, which shows the existence of relaxation in the dipole orientation process. A study of the frequency dependence enables the rotational mobility of the molecules to be determined and additional information to be obtained about their conformation and rigidity.

III. SOME EXPERIMENTAL RESULTS

1. Cellulose and Its Derivatives

As shown above, cellulose and its derivatives have for long been the best known, "classical" example of chain molecules with high skeletal rigidity. This property follows directly from the geometry of the molecular chain (Fig. 4).

The monomeric unit is a glucoside ring with two adjacent valence bonds OC_1 and OC_4, around which rotation is possible. In calculating the statistical dimensions of the chain its monomeric unit can be denoted[47] by an equivalent "effective" unit consisting of two parallel bonds $b = 2.7$ Å, around which rotation takes place and one bond $d = 1.45$ Å (normal to the first two) around which there is no rotation. On using this scheme it can be shown that for a sufficiently long chain with completely free rotation around bonds OC_1 and OC_4 (that is, "bonds" b) the mean square distance between its ends $\overline{h_f^2}$ is[47]:

$$\overline{h_f^2} = P[d^2 + (2b)^2(1 + \cos\vartheta)/(1 - \cos\vartheta)], \quad (27)$$

where P is the number of monomeric units in the chain, and $\pi - \theta$ is the valence angle between the neighbouring bonds OC_1 and OC_4.

On substituting the values of b and d and assuming $\theta = 70°$ we obtain $\overline{h_f^2} = 62P \times 10^{-16}$ cm^2, and for the length of a segment of the cellulose chain with completely free rotation:

$$A_f = \overline{h_f^2}/P\lambda = \overline{h_f^2}/P\left(2b\cos\frac{\vartheta}{2} + d\sin\frac{\vartheta}{2}\right) = 12 \text{ Å}.$$

This value of A_f corresponds with the number of monomeric units in the segment $S_f = 2.5$.

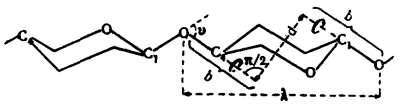


Figure 4. Conformation of the cellulose chain. λ = projection of the monomeric unit on the chain direction; $b = 2.7$ Å is the length of the "effective bond" around which rotation is possible; $d = 1.45$ Å is the length of the "effective bond" around which rotation is impossible.

For a carbochain polymer not containing rings in the chain under the condition of free rotation an analogous calculation gives[1]:

$$A_f = l(1 + \cos\vartheta)/(1 - \cos\vartheta)\sin\vartheta/2,$$

which for $\theta = 70°$ and $l = 1.54$ A leads to the value $A_f = 3.8$ Å.

Hence even when there is completely free rotation the segment length of the cellulose chain should be more than three times as great as the segment length of a flexible carbochain polymer.

An analogous conclusion can be reached by considering the possible conformations of another linear polysaccharide—amylose. However, here the theoretical values are less definite since spiral structures can be formed with amylose[48].

The real polymeric chains in a Θ-solvent have the undisturbed dimensions $(\overline{h_\Theta^2})^{\frac{1}{2}}$, which owing to restricted rotation exceed the chain dimensions in free rotation:

$$\overline{h_\Theta^2}/\overline{h_f^2} = \sigma^2,$$

where σ is the rotation restriction factor. Many flexible carbochain polymers are characterised by values of σ lying in the range $\sigma^2 \simeq 4$–5, which corresponds with segment lengths of $A = A_f\sigma^2 \simeq 15$–$20$ Å.[1,25,49]

The problem of the value of the restriction factor σ for cellulose derivatives has been the subject of discussion recently. The method with the best theoretical basis for determining σ is the direct measurement of the undisturbed radius of gyration of the molecule $\overline{R^2}$ from the asymmetry of its light scattering in solutions. There are considerable experimental difficulties in such measurements for polysaccharides[21-23] and evidently for this reason they are rather few. Some examples are given in Table 1. The values of $A = S\lambda$ were calculated from the experimental values of $\overline{R^2}/P = \frac{1}{6}S\lambda$, obtained in the range of limitingly large values of P, Eqns. (3) and (2′). Here the values of λ were taken as 5.15 and 3 Å for cellulose and anylose chains respectively (the value $\lambda = 3$ Å corresponds to a helical model of the amylose chain[48,50]). Corresponding values of the restriction factor $\sigma = (A/A_f)^{\frac{1}{2}}$ are given here.

The value of A for polysaccharides is an order of magnitude greater than the corresponding values found by the light scattering method for most of the flexible carbochain polymers[1]. The rotation restriction factor σ in polyglucose chains is, according to the light scattering results, at least twice the value of σ for flexible chain polymers[1,25,49].

Table 1. Segment length A, number (S) of monomeric units in the segment, and rotation restriction factor for molecular chains of some derivatives of polysaccharides obtained from measurements of the asymmetry of light scattering.

Polymer	Solvent	10^8A, cm	S	σ	Reference
Cellulose trinitrate	acetone	230	44	4.4	51
	acetone	235	45	4.4	52
	acetone	233	44	4.4	53
	ethyl acetate	234	44	4.4	54
	isopentyl acetate	216	42	4.25	53
	dioxan	220	43	4.3	53
	nitrobenzene	58	11.2	2.2	53
Cellulose tricarbanilate	dioxan–methanol mixture (Θ-solvent)	268	52	4.7	55
Amylose tricarbanilate	dioxan–methanol mixture (Θ-solvent)	414	80	5.8	55
Amylose acetate	nitromethane	100	19	2.9	56

Conclusions about the high rigidity of the molecules of cellulose derivatives[51-56] also agree with hydrodynamic properties of their solutions. Thus the index α in the Mark–Kuhn equation (5) for many of them is close[49] to unity, which is usually connected with the flow effect, whereas the excluded volume effect (ideality of the solvent) is less important[53,55].

At the same time it was noted in several studies[53,57-60] that certain properties of the solvent and the temperature have a pronounced influence on the undisturbed dimensions (that is, the skeletal rigidity) of the molecules of the cellulose derivatives.

In recent years another point of view on the rigidity of molecules of cellulose derivatives has been advanced, based on the use of viscosimetric results for the determination of their unperturbed dimensions[25]. Here it was suggested that the high value of the index α in Eqn. (5) and the large molecular dimensions observable experimentally in polysaccharides are the consequence not of their increased rigidity but of the exceptionally marked influence of the volume effects, since modern theories in principle admit a value of $\epsilon = \frac{1}{3}$ in Eqn. (4) and correspondingly $\alpha = 1$ in Eqn. (5) owing to the non-ideality of the solution[20]. A second a priori assumption, which is made in this is the postulation of almost complete non-flowability of molecules of cellulose derivatives in solutions, like the molecular coils of flexible chain polymers. On starting from this assumption the undisturbed dimensions of the molecules are determined from the viscosimetric results of the extrapolation of the latter into the range of low molecular weights, using Eqn. (8). The unperturbed dimensions and the restriction factor σ, obtainable as a result of such a

procedure are close to the corresponding values for flexible carbochain polymers and on this basis it is concluded that the molecular chains of cellulose and its derivatives do not exhibit a high rigidity[25,61-64].

Recently Flory[65] criticised this viewpoint by observing that in addition to an unproven neglect of the flow effect in molecules of cellulose derivatives it also ignores the departure from gaussian behaviour of their chains in the range of low molecular weights—factors, the presence of which makes the use of formula (8) quite improper. The reality of the pronounced influence of flow on the hydrodynamic properties of molecules has been demonstrated for several polysaccharides[66,67].

The departure from gaussian behaviour in the range of low molecular weights for polysaccharide chains has been shown in several papers[51-55] by the direct determination of their dimensions by the method of asymmetry of light scattering in solutions. This gave the dependence of the dimensions on the molecular weight which corresponded at least qualitatively to Eqns. (2) and (3) and to the theoretical curve (Fig. 1) for rigid wormlike chains.

Unlike flexible chain molecules[34-36], the dependence of the viscosity $[\eta]$ on the molecular weight M in the range of low M for cellulose derivatives also has features which show the absence of gaussian properties[68].

What has been stated above gives grounds for considering that the characteristic parameters of the rigidity of polysaccharide molecules found by direct measurements (Table 1) are much more reliable than the corresponding quantities obtained by use of model theories and making several doubtful assumptions[25,61-63].

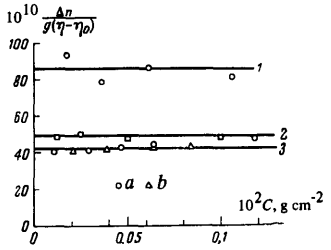


Figure 5. Reduced birefringence of solutions of cellulose monophenylacetate in various solvents depending on the concentration[69]: *1*) in ethyl acetate; *2*) in cyclohexanone; *3*) *a*) in bromoform; *b*) in acetophenone.

Because of the discussion and existence of two opposite viewpoints it is extremely important to obtain data on the rigidity of cellulose molecules by other methods free from model assumptions of hydrodynamic theories and independent of the thermodynamic properties of the solution. As already stated, a study of the dynamo-optical properties of the solutions can be such a method.

Usually the value of the flow birefringence and the corresponding optical anisotropy of a segment are appreciably greater for cellulose derivatives than for flexible-chain polymers[1], which by itself is a qualitative index of the high skeletal rigidity of polysaccharide chains.

In solutions of cellulose derivatives where the refractive index of the polymer n_k differs from the refractive index of the solvent n_s a very high form effect is observed.

It is characteristic that the reduced birefringence $\Delta n/\Delta\tau$ is here independent of concentration (see Fig. 5) unlike the marked concentration dependence of the form birefringence for solutions of flexible-chain polymers[1,43].

Another characteristic feature of the form effect, observable in solutions of cellulose derivatives, is the extremely weak dependence of the reduced birefringence $\Delta n/\Delta\tau = [n]/[\eta]$ on molecular weight (Fig. 6), whereas for flexible-chain polymers the value of $[n]/[\eta]$ increases sharply with the molecular weight (Fig. 7).

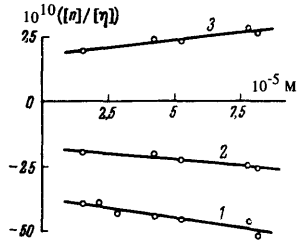


Figure 6. Variation of the reduced anisotropy of solutions of cellulose nitrate with the molecular weight[70]. *1*) $[n]/[\eta]$ for fractions of cellulose nitrate in cyclohexanone ($n_k - n_s = 0$, proper anisotropy); *2*) $[n]/[\eta]$ for the same fractions in butyl acetate ($n_k - n_s$, total birefringence); *3*) $[n]/[\eta]$ corresponding to the microform effect, calculated by subtracting the ordinate of curve *1* from the ordinate of curve *2*.

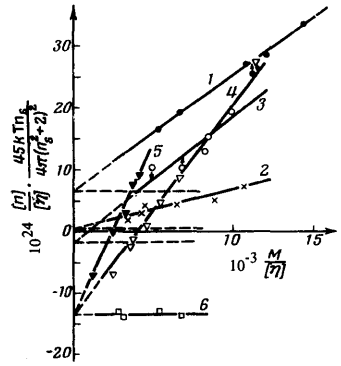


Figure 7. Variation of the quantity

$$x=\frac{[n]}{[\eta]}\cdot\frac{45kTn_s}{4\pi(n_s^2+2)^2},$$

which forms part of Eqns. (18) and (19) with $M/[\eta]$ for solutions of certain flexible-chain polymers[1]. *1*) Polyisobutene in hexane; *2*) polydimethylsiloxane in toluene; *3*) poly(butyl methacrylate) in ethyl acetate; *4*) polystyrene in dioxan ($n_k - n_s = 0.18$); *5*) polystyrene in butanone ($n_k - n_s = 0.22$); *6*) polystyrene in bromoform ($n_k - n_s = 0$).

Both the first and the second feature show that the form birefringence observable in solutions of cellulose derivatives (unlike flexible chain molecules) is an effect of the chain microform and determinable by Eqn. (20).

In accordance with Eqn. (20) the experimentally found variation of $[n]/[\eta]$ with the refractive index of the solvent n_S is a parabolic curve (Fig. 8). The minimum of the parabola gives the proper anisotropy of the segment $\alpha_1 - \alpha_2$. From the remaining points of the curve, using Eqn. (20), the molecular weight of the segment $M_S = A(M/L)$ can be calculated and hence its length A. The values thus obtained for certain cellulose esters are given in Table 2.

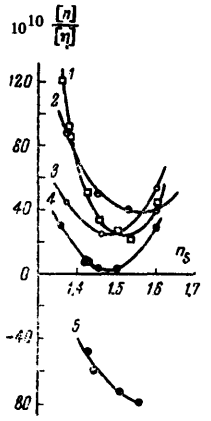


Figure 8. Variation of the reduced birefringence $[n]/[\eta]$ of solutions of cellulose esters with the refractive index of the solvent: *1*) cyanoethyltritylcellulose[73]; *2*) monophenylacetylcellulose[69]; *3*) ethyl cellulose[71]; *4*) cyanoethylacetylcellulose[72]; *5*) cellulose benzoate[69].

For specimens 3, 4, and 5 with large lateral substituents $(L_2 - L_1)_S = 2$ is taken for calculating A, for the other specimens $(L_2 - L_1)_S = 2\pi$.

As Table 2 shows, the segment lengths A and the corresponding values of σ obtained by measuring the flow birefringence have magnitudes close to the values of A and σ found by the light scattering method (Table 1). Similar results are given by an investigation of the photoelasticity of gels of cellulose derivatives in various solvents[72,73].

Hence the dynamo-optical properties of solutions and gels of cellulose derivatives are not only a qualitative but also a quantitative index of the high skeletal rigidity of their molecular chains.

This rigidity is determined not only by the presence of rings in the chain—a high value of $\overline{h_f^2}$ in Eqn. (27) and hence of A_f—but also by the higher (than for carbochain molecules) value of the restriction factor σ. It is very probable that a significant part in the retardation of intramolecular rotation is played by the hydrogen bonds established between the oxygen, hydrogen, and nitrogen atoms forming part of the lateral substituents of the polyglucose chain.

For polysaccharide molecules containing ionogenic groups the skeletal rigidity can be increased even more, owing to the electrostatic interaction of these groups.

A decrease in the ionic strength of the solution and an increase in the dissociation of the ionogenic groups is accompanied by the uncoiling of the chain of the polyion due to the electrostatic repulsion of its charged parts. During this there is an increase in both the characteristic viscosity of the solution (owing to the increase in the size of the molecular coils), and in its characteristic flow birefringence $[n]$. However, $[n]$ increases more rapidly than $[\eta]$ and therefore the ratio $[n]/[\eta]$ increases. This shows that in a polyelectrolytic uncoiling of a molecular chain of a polyion (unlike its osmotic swelling in a strong solvent) there is an increase in the segment anisotropy $\alpha_1 - \alpha_2$, Eqn. (18), and consequently also in the segment length A.

Table 2. Optical anisotropy and parameters of the rigidity of various cellulose esters from the flow birefringence.

Polymer	Degree of substitution	$(\alpha_1 - \alpha_2)\cdot 10^{25}$, cm^3	$10^8 A$, cm	s	$(\alpha_\parallel - \alpha_\perp)\cdot 10^{25}$, cm^3	$\sigma = \left(\frac{\overline{h_0^2}}{\overline{h_f^2}}\right)^{1/2}$	Reference
Cellulose nitrate	2.60	−300	260	50	−12	4.7	70
Ethyl cellulose	2.60	310	180	35	18	3.9	71
Cellulose benzoate	3.0	−900	270	52	−36	4.8	69
Cellulose phenylcarbanilate	1.9	−1100	180	35	−60	3.9	69
Monophenylacetyl cellulose	2.5	440	250	49	18	4.6	69
Cyanoethylacetyl cellulose	1.7 0.9	15	250	49	0.7	4.6	72
Cyanoethyltritylcellulose	2.0 1.0	220	280	54	8	4.9	73

In other words, polyelectrolytic uncoiling of the chain is accompanied by an increase in its skeletal rigidity.

This is shown by Table 3, which gives the results of viscosimetric and dynamo-optical investigations of aqueous solutions of the sodium salt of a specimen of a sulphite ester of cellulose (Na-SC with a lateral substituent $-SO_3Na$, molecular weight $M = 10^5$) at various ionic strengths I.

Table 3. Hydrodynamic, optical, and conformational characteristics of the molecule of the sodium salt of sulpho-ester of cellulose at various ionic strengths of the solution[74].

I, M	$[\eta]$, cm^3 g^{-1}	$10^{10}\frac{[n]}{[\eta]}$	$10^{25}(\alpha_1 - \alpha_2)$, cm^3	$10^{25}\frac{\alpha_1 - \alpha_2}{[\eta]}$, g	$10^8 A$, cm
0.200	290	46.6	634	2.19	195
0.150	290	47.4	645	2.22	195
0.100	310	50.0	680	2.19	216
0.010	500	72.0	980	1.96	330
0.005	610	96.7	1320	2.16	410
0.001	870	127.0	1730	2.00	575

From Table 3, clearly the value of the ratio $(\alpha_1 - \alpha_2)/[\eta]$ is approximately the same for different ionic strengths and is equal to 2.1×10^{-25}. Because of the identity

$$\alpha_1 - \alpha_2 \equiv \beta_0 A$$

and Eqn. (1), we have

$$\overline{h^2}/[\eta] = 2.1 \cdot 10^{-25} \ (L/\beta_0).$$

for all ionic strengths. This signifies that (since for a particular chain molecule L/β_0 is independent of its convolution) in the polyelectrolytic uncoiling of the Na-SC chain the characteristic viscosity $[\eta]$ increases in proportion to $\overline{h^2}$, which is characteristic for hydrodynamically flowing gaussian coils. Therefore the assumption about the non-flowability of molecules of ionogenic derivatives of cellulose made in some studies[20,61,62] is untenable.

Judging by the structure of substituent groups, it can be expected that the proper segment anisotropy Na–SC in the range of high ionic forces ($I = 0.2$), when the polyelectrolytic effects are suppressed is close to the proper anisotropy of an ethylcellulose segment[71] $(\alpha_1 - \alpha_2)_i = 310 \times 10^{-25}$ cm^3. The fact that in aqueous salt solutions at $I = 0.2$ the observed anisotropy $(\alpha_1 - \alpha_2)$ is 634×10^{-25} cm^3, that is, is 634/310 = 2.05 times the value of $(\alpha_1 - \alpha_2)_i$, shows that half the birefringence thus observable is due to the microform effect. Starting from this and using Eqn. (20) the segment length A can be calculated. The values of A obtained at various ionic strengths (Table 3) show the increase in the skeletal rigidity of the chain during its polyelectrolytic uncoiling.

2. Molecules with a Regular Secondary Structure

a. Deoxyribonucleic acid (DNA). DNA, like cellulose derivatives, can be regarded as a classic example of a polymer with semirigid chain molecules. The generally accepted model of the molecule is the rigid double-helix structure proposed by Watson and Crick[75], maintained by hydrogen bonds, which "reinforce" the purine and pyrimidine bases of the DNA chain.

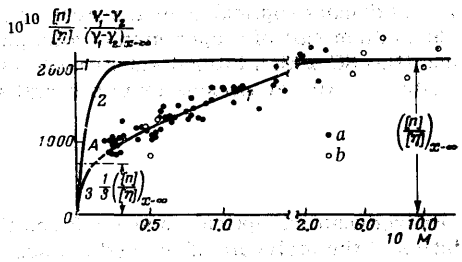


Figure 9. Flow birefringence $[n]/[\eta]$ and optical anisotropy of the DNA molecule as a function of molecular weight M. *1*) The curve of $[n]/[\eta] = f(M)$ drawn according to the experimental points; *a*) DNA fragment obtained by treatment of the DNA solutions; *b*) fragments obtained by ultrasonic destruction; *2*) curve for the variation of the relative anisotropy of the molecule $(\gamma_1 - \gamma_2)_L/(\gamma_1 - \gamma_2)_{x\to\infty}$ with $x = L/a$; *3*) initial part of the theoretical curve *2* of Fig. 2.

The application of the hydrodynamic theory of wormlike chains to the experimental results on sedimentation, Eqn. (12), leads to the values of the segment length A = 700–900 Å,[30–32] which is two to four times the value obtained for cellulose derivatives (Tables 1–3). The optical anisotropy of the DNA molecule found from the flow birefringence is very high and negative in sign. This corresponds to the high degree of orientation order of the base, the plane of which is perpendicular to the axis of the molecule.

The optical anisotropy increases with the molecular weight of DNA[76] in accordance with the theory of persistent chains[44] (Fig. 9). A comparison of the experimental curve with the theoretical one, Eqn. (22), leads to the value A = 600 Å.[76]

b. Polypeptides $-\overset{\overset{O}{\|}}{C}-CHR-\overset{\overset{H}{|}}{N}-$ Polypeptides in a helical conformation are a good example of a rigid-chain molecule with a very high rigidity. The most complete information about the hydrodynamic, optical, and electrical properties of molecules was obtained for poly-γ-benzyl-L-glutamate (PB-L-G).

The high rigidity of spiral molecules is best shown by the high value of the exponents α and β in the Mark-Kuhn equations (5)–(7).[33,46,78]

Experimental results on diffusion and sedimentation have been used for the quantitative determination of rigidity. Fig. 10 shows the variation of the sedimentation coefficient $[s]$ or the quantity DM/RT with the square root of the molecular weight $M^{\frac{1}{2}}$. According to Eqn. (12) the slope of the straight line obtained leads to a value of 2200 Å for the segment length A.[33,46] The flow birefringence in solutions of α-spiral polypeptides is very high and increases with the molecular weight (Fig. 11). Use of this relation and the theory of persistent anisotropy[44], Eqns. (21) and (22), lead to values for the anisotropy and length of the segment of respectively $\alpha_1 - \alpha_2 = 20\,000 \times 10^{-25}$ cm^3 and A = 2400 Å.

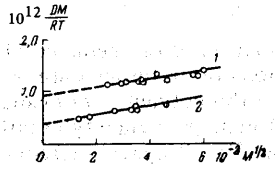


Figure 10. Variation of DM/RT with $M^{\frac{1}{2}}$ for poly-γ-benzyl-L-glutamate (*1*) and poly(butylisocyanate) (*2*).

These values agree with the hydrodynamic values and show the high degree of intramolecular orientation ordering Q, determined from Eqn. (23).

A comparison of the curves in Figs. 3 and 11 shows that in the molecular weight range investigated the value of Q for the PB-L-G molecules varies in the range 0.35–0.8, that is, it corresponds with the level of the orientation order characteristic for the nematic mesophase. Therefore the PB-L-G molecules are typical examples of a "crystal-like" molecule.

In an electric field a high birefringence arises in the PB-L-G solutions, showing the high degree of orientation-dipole order in the molecule. The positive sign of the Kerr effect shows that the total dipole moment of the molecule is directed along its axis, being the sum of the local moments of the C=O...H–N group joined by hydrogen bonds.

A comparison of the dynamo-optical and electro-optical results, Eqns. (22) and (24), enables the segment length A to be determined. The value A = 1400 Å thus obtained[46] is less than that found from the results of measurement of diffusion, sedimentation, and flow birefringence.

This fact shows that the processes in the orientation of polar polypeptide molecules in mechanical and electric fields cannot be identified. There is evidently a significant difference in the degrees of the axial and polar correlations of the units of the polypeptide helix chains.

The high value of the optical anisotropy and dipole moments are characteristic only for polypeptide molecules in

a helical conformation maintained by hydrogen bonds. When the latter are broken in strong solvents, in addition to the breakdown of the spiral structure the crystal-like orientation ordering is also destroyed and furthermore there is almost complete disappearance of the large optical effects observable in mechanical and electrical fields. An illustration is given by Figs. 12 and 13, which show the changes in birefringence in flow and in an electric field and the viscosity of the PB-L-G solution during the spiral–coil intramolecular conformational transformation[104].

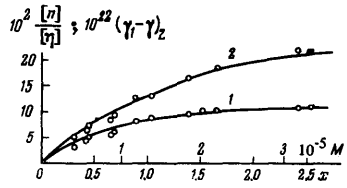


Figure 11. Variation of the reduced anisotropy of the solution $\Delta n/g(\eta - \eta_0) = [n]/[\eta]$ (*1*) and $\gamma_1 - \gamma_2$ (*2*) with the molecular weight for fractions of poly-γ-benzyl-L-glutamate in dichloroethane.

3. Polymeric Molecules with Rings in the Main Chain

The rigidity of the spiral conformation of polynucleotides or polypeptides is maintained by hydrogen bonds formed by intramolecular cyclic parts of the chain and leading to a "lattice" structure of the molecule.

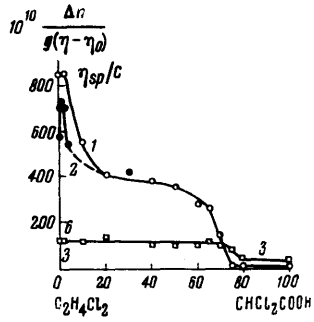


Figure 12. Variation of the optical anisotropy (*1* and *2*) and viscosity (*3*) of a solution of poly-γ-benzyl-L-glutamate during the destruction of the helical structure of the molecule. Solvent: *1*) dichloroethane—2% dimethylformamide with the addition of dichloroacetic acid; *2*) dichloroethane with the addition of dichloroacetic acid.

It could be expected that the same result can be reached for synthetic chain polymers by the introduction of heterocycles, some atoms of which enter the main chain of the polymer.

Although a large number of polymers with heterocycles in the chain have been obtained in recent years[79-82], quantitative data about the conformation and rigidity of such molecules in the solutions are very few. One of the probable reasons for this is the poor solubility of such polymers in ordinary solvents.

Detailed quantitative data about the properties of the solutions were obtained for polymers of N-substituted maleimides[83], which are readily soluble in organic solvents and occupy a sufficiently wide range of molecular weights[84].

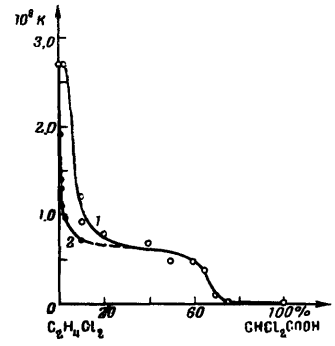
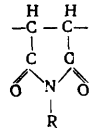


Figure 13. Variation of the Kerr constant (K) of a solution of poly-γ-benzyl-L-glutamate during the destruction of the helical structure of the molecule. Solvent: *1*) dichloroethane–dimethylformamide with the addition of dichloroacetic acid; *2*) dichloroethane with the addition of dichloroacetic acid.

a. Poly-N-isobutylmaleimide[84] (PIBMI)



As follows from the structural formula of this polymer, the presence of imide rings halves the number of single bonds around which rotation in the main chain is possible. In accordance with this, increased rigidity of the molecular chain can be expected. The rigidity of the chain was determined from the experimental results on sedimentation, diffusion, and viscometry. To rule out the influence of volume effects and to determine the undisturbed dimensions of the molecule, the hydrodynamic results were extrapolated to limitingly small molecular weights in accordance with Eqns. (8) and (10). Such a construction is shown in Fig. 14 for fractions of PIBMI in butyl acetate. The intercepts made by the straight lines on the ordinate axis give for the length of the Kuhn segment the value A = 35–40 Å, which is twice the value usually obtained for flexible chain volumes without rings in the chain[1].

However, the doubling of the rigidity due to cyclisation of the chain is not high enough for the molecule concerned to be classified as semirigid from its behaviour in solution. Thus the values of the indices $\alpha = 0.65$ and $\beta = 0.59$ in the M–K formulae (5–7) for PIBMI molecules (which are greater than 0.5) are due to the excluded volume effects and hence are unconnected with the increased rigidity of the chain. In accordance with this the anisotropy of the molecules and the reduced birefringence $[n]/[\eta]$ for PIBMI solutions in the investigated range of molecular weights

corresponds to the Kuhn equations (14) and (18) for gaussian chains and does not depend on the molecular weight[84].

Hence to reduce the flexibility of the chain to a value characteristic for semirigid chain molecules the fraction of the cyclised chains should be appreciably greater than one-half. Complete cyclisation of all the chains gives the limitingly rigid structure of the "staircase" polymer.

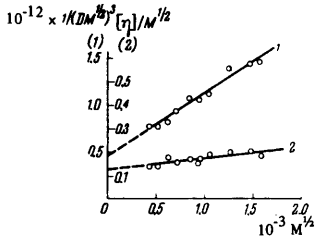
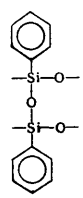


Figure 14. Variation of the quantities $(1/DM^{\frac{1}{2}})^3$ (*1*) and $[\eta]/M^{\frac{1}{2}}$ (*2*) with $M^{\frac{1}{2}}$ for fractions of poly-*N*-isobutylmaleimide in butyl acetate.

b. Staircase polyphenylsiloxane [85].



This polymer has been obtained by several investigators [86,87]. Fig. 15 shows the probable structure of its molecule. Here the cyclisation is effected by transverse Si–O bonds, which strengthen the two siloxane chains. Study of the hydrodynamic properties of fractions of one of the specimens in solutions leads to M–K dependences (5)–(7), in which the indices greatly exceed 0.5 ($\alpha = 0.88$, $\beta = 0.63$). [85]

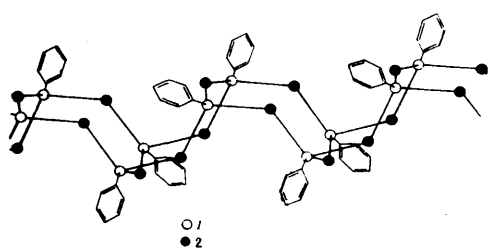


Figure 15. Structure of the molecule of staircase polyphenylsiloxane: *1*) silicon atoms; *2*) oxygen atoms.

This is due to the considerable skeletal rigidity (the flow effect) whereas the role of the excluded volume effects is small and cannot be considered.

In accordance with this the rigidity of the chain can be determined by constructing the variation of $[s]$ with $M^{\frac{1}{2}}$ and of $M/[\eta]$ with $M^{\frac{1}{2}}$ shown in Fig. 16 for one of the specimens of a staircase polymer. The slopes of the straight lines obtained lead, by use of the theory—Eqns. (11) and (12)—to values of A = 200 Å for the segment length. This value is ten times the value of A for the chain molecules of a staircase polyphenylsiloxane without rings in the chain. [1] The considerable rigidity of the molecule of the staircase polymer is quite adequate for the appearance of properties characteristic for semirigid chain molecules in the molecular weight range investigated.

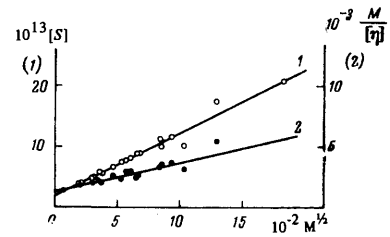


Figure 16. Variation of the quantities $[s]$ (*1*) and $M/[\eta]$ (*2*) with $M^{\frac{1}{2}}$ for fractions of staircase polyphenylsiloxane.

These properties are shown clearly in the optical behaviour of the solutions. In these there is great negative flow birefringence (which corresponds to the sign of the anisotropy introduced by the lateral phenyl radicals), the reduced value of which increases with the molecular weight (see Fig. 17) in complete agreement with the theory of the anisotropy of persistent chains—Eqns. (21) and (22).

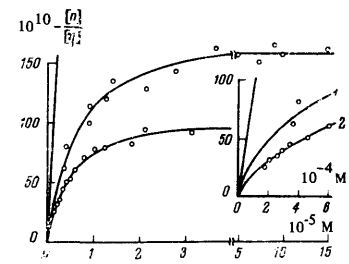


Figure 17. Variation of the reduced birefringence $[n]/[\eta]$ with the molecular weight M for fractions of two specimens of staircase polyphenylsiloxane: *1*) specimen 1; *2*) specimen 2. The experimental points correspond with the following values of the persistent length and anisotropy: for specimen 1) a = 90 Å, $\alpha_1 - \alpha_2 = -1.8 \times 10^{-22}$ cm^3; for specimen 2) a = 50 Å, $\alpha_1 - \alpha_2 = 1 \times 10^{-22}$ cm^3.

The segment length A, estimated from the initial slope and the asymptotic limit of the experimental curves of Fig. 17, is 180 Å, which agrees with the values obtained from hydrodynamic results.

The anisotropy of the segment, determinable from the asymptote of curve *1*, Fig. 17, is $\alpha_1 - \alpha_2 = -1800 \times 10^{-25}$ cm^3, which is 20 times the anisotropy of linear isotactic metaphenylsiloxane without rings in the chain [88].

At the same time the fractions $\Delta\alpha$ introduced into the anisotropy of the molecule by a single phenyl ring are almost the same for staircase and linear single-chain polyphenylsiloxanes ($\Delta\alpha = -20 \times 10^{-25}$ cm^3). This indicates that transverse oxygen bridges, which strengthen the double chain molecule of the staircase polymer and greatly increase its skeletal rigidity, are without any significant effect on the rotational mobility of the lateral phenyl groups.

Although the rigidity of the molecule of a staircase polymer is great, it is completely terminal and close, for example, to the rigidity of the chains of the cellulose esters. At a molecular weight of about 100 000 the molecule is already a gaussian coil in several of its properties, that is, considerable rigidity appears. A comparison of the curves of Figs. 17 and 3 shows that for the fractions investigated the degree of intramolecular ordering Q lies in the range from 0.2 to 0.005, that is, considerably below the level of organisation of a smectic mesophase.

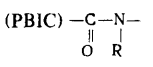
It should be noted that in the example of a staircase polymer we encounter a mechanism for chain rigidity which is greatly different from that for linear chain molecules without a secondary structure. Here the flexibility is due not to restricted rotation around valence bonds (or rotational isomerism) but to microdeformations of the macromolecular "lattice" in its thermal vibrations. However, local defects of the intramolecular lattice probably play some part in this. An illustration of this is provided by curve *2* of Fig. 17, which shows the relation $[n]/[\eta] = f(M)$ for the fractions of a specimen of cyclolinear polyphenylsiloxane obtained under somewhat different conditions than for specimen *1*. Although this polymer undoubtedly has a staircase structure, which appears in its hydrodynamic and optical properties, the presence of local defects in the structure of the molecule diminishes its rigidity and anisotropy to the values $A = 100$ Å and $\alpha_1 - \alpha_2 = -1060 \times 10^{-25}$ cm^3 respectively.

The rigidity of the molecule of a staircase polymer can be markedly decreased by the creation of "chemical" defects in its lattice, for example, by the introduction of single bonds into the molecular chain. Such partial "decyclisation" of the molecule leads to a partly staircase structure[89,90]. The poly-(*N*-isobutylmaleimide) considered above can evidently serve as an example of a "semistaircase" polymer.

The conformational properties of the molecules of other possible partial-staircase polymers have not been studied.

4. Molecules with Resonance Interaction in the Chain

The presence of additional intramolecular bonds (hydrogen or chemical), which "cyclise" the structure and thus ensure its rigidity is characteristic of all the above polymers with rigid chain molecules. Until comparatively recently it could have been thought that these structural properties are a necessary condition for the existence of semirigid chain molecules. However, the synthesis of polyisocyanates[91,92] and the study of the properties of their solutions[93-96] shows this to be incorrect. It was shown that the molecules of certain polyalkylisocyanates in solution have exceptionally high rigidity and ordering of the structure. The polybutyl isocyanate



where R = C_4H_9, was investigated in the most detail.

Solutions of this polymer in non-polar solvents are characterised by high values of the exponents α and β ($\alpha = 1.2$; $\beta = 0.85$) in the Mark–Kuhn equations (5)–(7).

To illustrate the great rigidity of the PBIC molecule, the viscosimetric results obtained for it can be treated[96] using the main formulae of the theory of viscosity of solutions of rigid ellipsoids:

$$[\eta] = \bar{v}\nu(p);\ H^3 = 6p^2\bar{v}M/\pi N_A\ . \qquad (28)$$

where $p = H/d$; H and d are respectively the long and short axes of the ellipsoid modelling the molecule, $\bar{v}$ and M the partial specific volume and molecular weight of the polymer, and $\nu(p)$ the viscosity increment, a function of the asymmetry p of the ellipsoid, tabulated by Simha[1].

The values of $d = H/p$ and H/Z calculated by Eqn. (28) and the experimental values of $[\eta]$, $\bar{v}$, and M are shown in Fig. 18 as functions of the degree of polymerisation Z. The decrease in H/Z and the increase in d with increase in Z show the considerable flexibility of the chain and the departure of its form (with increase in Z) from rod-shaped. However, the limiting values of $H/Z = 2 \times 10^{-8}$ cm and $d = 11 \times 10^{-8}$ cm agree reasonably with the length and diameter of the monomeric unit of the molecular chain of PBIC.

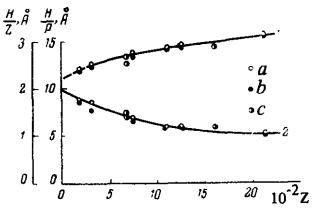


Figure 18. Variation of the quantity $H/p = d$ (*1*) and H/Z (*2*) with the degree of polymerisation Z for poly(butyl isocyanate) fractions in various solvents: *a*) benzene[93]; *b*) tetrahydrofuran[93]; *c*) benzene[96].

It follows from this analysis that in a range of molecular weights of a few tens of thousands (Fig. 18) the form of the PBIC molecule is close to a straight rod.

An analysis of the results on diffusion and sedimentation using the theory of wormlike chains—slope of the straight line *2* in Fig. 10, and Eqn. (12)—leads[96] to the enormous segment length A of 3000 Å, which surpasses even the segment length of the helical polypeptide molecules. The results on flow birefringence, which is very high and positive in solutions of polybutyl isocyanate, lead to similar conclusions.

The use of the microform effect, Eqn. (20), enables the segment length to be determined; the value obtained $A = 2600$ Å is close to the value found from hydrodynamic data. The anisotropy of the segment is great ($\alpha_1 - \alpha_2 = 9000 \times 10^{-25}$ cm^3) and its magnitude is close to the anisotropy of helical polypeptide molecules.

In PBIC solutions there is also an extremely large positive electrical birefringence[96], which shows the existence in the molecule not only of axial but also of polar orientation ordering.

The pronounced frequency dependence of the Kerr effect (Fig. 19) is also proof of high rigidity (both equilibrium and kinetic) and of the ordering of the structure; it can be

used for determining the orientation relaxation time and the geometric parameters of the molecule[96].

The effect of the saturation of the electrical birefringence observed in strong fields (Fig. 20) shows the high value of the molecular dipole and can be used for determining the dipole moment μ of the molecule[96]. The values obtained are close to the values of the dipole moments of the polypeptide molecules in the helical conformation. Similar results are obtained from a comparison of the dynamo-optical and electro-optical results[96].

The values of the dipole moments of the molecules μ obtained from measurements of the dielectric properties of the solutions[95] can also be used for determining the segment length. Having constructed a plot of μ^2/L against L, we obtain the curve of Fig. 21. In accordance with theory—Eqn. (26)—the initial slope gives the square of the dipole moment of unit length of the persistent chain $(\mu_S/A)^2$. The ratio of the asymptotic limit to the initial slope gives the segment length A. The value found by this method, A = 3000 Å, agrees with the value obtained from hydrodynamic results.

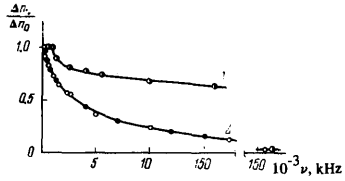


Figure 19. Variation of the relative value of the electric birefringence $\Delta n_\nu/\Delta n_0$ with the frequency ν for solutions of poly(butyl isocyanate) in tetrachloromethane: *1*) $M = 1.6 \times 10^5$; *2*) $M = 0.66 \times 10^5$.

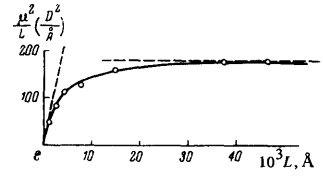


Figure 21. Variation of μ^2/L with L for poly(butyl isocyanate) in benzene.

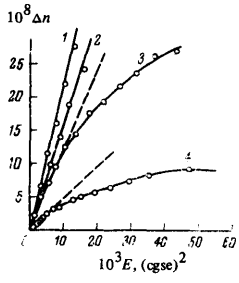


Figure 20. Variation of the electric birefringence with the square of the field strength E^2 for solutions of poly(butyl isocyanate) and poly(tolyl isocyanate) in bromoform (c = 1.77 g dl^{-1}); *3*) and *4*) poly(tolyl isocyanate) in tetrachloromethane (specimen 3; $M = 1.6 \times 10^5$, $c = 0.6 \times 10^{-3}$ g dl^{-1}); (specimen 4: $M = 0.66 \times 10^5$, $c = 0.7 \times 10^{-3}$ g dl^{-1}).

Table 4 summarises the molecular characteristics of PBIC. All these experimental results taken together show that the conformation of the PBIC molecule in weakly polar solvents corresponds to the wormlike chain model. The rigidity and ordering of its structure determined by various methods are very great and close to the rigidity and ordering of the molecules of synthetic polypeptides having an α-helical secondary structure. On taking into account the value found above for A and using Fig. 3 it is clear that for the fractions shown in Fig. 18 the value of Q lies in the range $0.4 \leq Q \leq 0.9$. Hence the PBIC molecules are crystal-like molecules with a very high degree of orientation order. Similar properties were observed in the polymers of other substituted alkyl isocyanates—polyhexyl isocyanate[94] and poly(chlorohexyl isocyanate)[96].

The chemical structure of the molecules of polyisocyanates are similar to the structure of polypeptide molecules, but the hydrogen atom in them is replaced by a side chain and the CHR group is absent from the main chain. The first feature (the absence of an N–H bond) rules out the possibility of the formation of a rigid α-helix conformation, since there are no intramolecular hydrogen bonds.

Table 4. Structural characteristics of molecules of some rigid-chain polymers.

Polymer	Mechanism of rigidity	10^{-5}M	$10^8 A$ cm	$10^{25}(a_1 - a_2)$ cm^3	$10^{23}(a_\parallel - a_\perp)$ cm^3	$10^{18}\mu$ cgse	Q
Polystyrene (for comparison)	restriction of rotation	1—100	20	—140	—18	—	$5 \cdot 10^{-3}$—$3 \cdot 10^{-5}$
Polybutylmaleimide	semistaircase structure	1.9—34	40	160	10	—	$8 \cdot 10^{-3}$—$4.4 \cdot 10^{-4}$
Polyphenylsiloxane	staircase structure						
Specimen 1		0.36—33.5	180	—1800	—25	—	0,42—$4.8 \cdot 10^{-3}$
Specimen 2		0.17—3.11	100	—1060	—25	—	0,34—0.02
Deoxyribonucleic acid	secondary helical structure	0.2—110	800	—40000	—200	—	0,41—$8.5 \cdot 10^{-3}$
Poly-γ-benzyl-*L*-glutamate	secondary helical structure	0.4—3.4	2400	20000	17	150—370	0.88—0.41
Poly(butyl isocyanate)	resonance interaction of the chain	0.2—2.0	3000	9000	7	253—2900	0.89—0.40
Phenylmethacrylic ester of cetyloxybenzoic acid	interaction in side-chains	18	65	—2700	—100	30	$3.1 \cdot 10^{-3}$
Graft copolymer of styrene and methyl methacrylate	interaction in side-chains	2.0—50	100	750		—	0.12—$0.48 \cdot 10^{-3}$

The second feature can have a decisive importance in the stabilisation of the rigidity of the molecular chain. Actually, since the peptide bonds in the polyisocyanate molecule are not separated by CHR groups, the coplanarity of all the bonds inside one peptide group (–CO–NR–) can be extended to each neighbouring pair of peptide groups, ensuring a rigid conformation of the whole chain. Here the resonance interaction of each nitrogen atom is extended to both carbonyl groups adjacent to it, giving the C–N bonds the rigidity of conjugated bonds[94].

Of the two possible planar structures of the chain (Fig. 22) the more probable is the *cis*-form, since it alone ensures the presence of a molecular dipole moment parallel to the axis of the molecule, and, corresponding to this, the agreement of the signs of the electrical and dynamic birefringences[96].

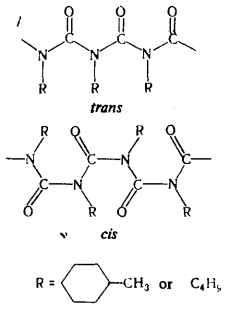


Figure 22. *trans*- and *cis*-conformations of polyisocyanate chains.

Hence poly(alkyl isocyanates) are unique instances when the exceptionally high rigidity of the conformation and the high degree of intramolecular ordering of the chain molecule are due not to the secondary structure but to the true skeletal rigidity of its single-track chain.

In addition to giving rise to these properties the structure of the side-radical at the nitrogen atom plays an important part. Thus replacing an aliphatic by an aromatic radical (tolyl isocyanate)[96] leads to the breakdown of the unique structure of the molecule. The reason for this can be sought both in the weakening of the resonance interaction in the nitrogen–carbonyl system owing to the effect of conjugated bonds of the aromatic ring and in the steric repulsion of neighbouring tolyl side-groups.

5. Molecules with Chain Side-radicals

The effect of the size and structure of the side-groups on the conformation of the polymeric molecules and the rigidity of their main chains has been studied repeatedly. Although in principle such an influence should occur the effects observable experimentally always appear insignificant[1].

Some new information about this problem was obtained recently in connection with the study of the conformational and optical properties of chain molecules having a "comb-shaped" structure. The latter is inherent to molecules with sufficiently long (linear) side-radicals or can be obtained by the grafting of one chain polymer on to another. However, in every instance the side-groups should be much shorter than the main chain.

A new approach to the study of the conformations of such molecules consists in the application of the theory of persistent anisotropy to the optical properties of the side-groups and in the calculation of their optical anisotropy in the axes of their primary element[38,44].

On drawing a tangent to the initial element of the persistent chain of length L and denoting the polarisability of the chain in the directions parallel and perpendicular to it by $\gamma_{\parallel}$ and $\gamma_{\perp}$ respectively, then for the difference $(\gamma_{\parallel} - \gamma_{\perp})_L$ the theory gives

$$(\gamma_{\parallel} - \gamma_{\perp})_L = \frac{1}{3} a\beta_0 (1 - e^{-3x}) = a\beta_0 x \left(1 - \frac{3}{2}x + \frac{3}{2}x^2 - \right.$$
$$\left. - \frac{9}{8}x^3 + \frac{27}{40}x^4 - \frac{27}{80}x^5 + \ldots\right). \quad (29)$$

The symbols in Eqn. (29) agree with those used in Eqn. (21).

The dependence of the ratio $(\gamma_{\parallel} - \gamma_{\perp})_L / \alpha\beta_0$ on the parameter x is shown in curve *3* of Fig. 2. The initial slope and asymptotic limit of the curve are respectively 1 and 1/3.

A comparison of curves *3* and *1* of Fig. 2 shows that the anisotropy of the gaussian chain (at $x \to \infty$), calculated using the axes of its primary element is 5/18 of the anisotropy calculated using the axes of vector h.

The application of Eqn. (29) to the anisotropy of the side-chain of the comb-shaped molecules shows that the contribution Δb_L introduced by the side radical to the anisotropy of the monomeric unit of the molecule is:

$$\Delta b_L = -S^* \cdot \Delta a \,(1 - e^{-6n/S^*})/12 \quad (30)$$

where n and S^* are the numbers of valence bonds in the side-chain and in its segment respectively, Δa the anisotropy of the part of the side-chain containing one valence bond.

Hence from the contribution made by the side-chain groups to the anisotropy of the whole molecule the anisotropy and flexibility of these groups can be studied by the above method.

a. Poly-α-alkenes $-\overset{R}{\underset{|}{C}}H-CH_2-$ $(R = C_nH_{2n+1})$

tematic experimental results on the dependence of the anisotropy of molecules on the number n of methylene groups in its side-radicals have been obtained for a number of poly-alkenes[97]. It was shown that in several poly-α-alkenes the lengthening of the side-group is accompanied by a monotonic rise in the negative anisotropy of the segment of the molecule $\alpha_1 - \alpha_2$. This increase can be caused both by increase in rigidity of the main-chain (an increase in A or S) and also by an increase in the negative contribution introduced into the anisotropy of the monomeric unit of the molecule by its side-group with lengthening of the latter.

If the change in the rigidity of the main-chain in the lengthening of the side-group is neglected (which is true only for the lower homologues of the series), then the experimentally obtained dependence can be represented in the form $\Delta b_L = 2.73 \times 10^{-25} n$ cm^3. On the other hand if it is assumed that the flexibility of the lateral hydrocarbon chain of the molecule of the poly-alkene equals the flexibility of the polyethylene chain, then assuming that $S^* = 16$,[1] from Eqn. (30) we obtain the theoretical relation $\Delta b_L = -7.3 \times 10^{-25}(1 - e^{-3n/8})$. Both relations are shown in Fig. 23.

The theoretical curve shows that owing to the flexibility of the side-chain with increase in its length (that is, n) the anisotropy of Δb_L should reach an asymptotic limit determinable from the degree of flexibility of the side-groups.

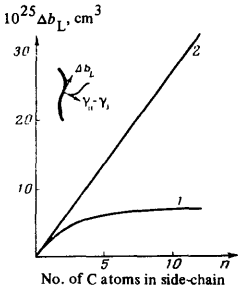
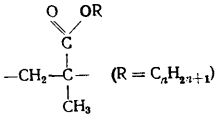


Figure 23. Contribution Δb_L introduced by the side-group to the anisotropy of the monomeric unit of a poly-α-alkene molecule as a function of the number (n) of carbon atoms in the side-chain. *1*) Theory of non-interacting chains with a flexibility equal to the flexibility of a polyethylene chain $\Delta b_L = 7.3 \times 10^{-25}(1 - e^{-3/8n})$ as follows from Eqn. (30); *2*) $\Delta b_L = 2.73 \times 10^{-25} n$ (see experimental results of Ref. 3).

However, in the range of values of n studied the experimental relation shows no tendency to saturation. This shows that the rigidity and orientation ordering of the side-groups of poly-α-alkenes greatly exceed the values which can be obtained from the experimental investigation of the conformational and optical properties of the individual hydrocarbon chains in the solution.

b. Poly(alkyl methacrylates).



A study of the conformation and optical anisotropy of the molecules of several poly(alkyl methacrylates) leads to similar conclusions[28]. Unlike the poly-α-alkenes, in addition to optical data results for this series were also obtained about the statistical dimensions and rigidity of the main-chain[28,98,99]. Consideration of these results can include more quantitative results than in the previous instance.

The experimental results on the rigidity of the main-chain and the anisotropy of the molecules of the poly(alkyl methacrylates) are given in Table 5. Up to $n = 8$ the length of the side-group has little effect on the rigidity of the main chain (the number of monomers S in its segment is close to 7–8). With a further growth of the side-chain the rigidity of the main chain increases considerably and at $n = 16$ is already twice that of molecules of the usual flexible chain polymers. This increase must evidently be regarded as the result of the interaction of long side-radicals of the molecule.

A much steeper expression of the increase in the negative anisotropy of the molecular segment $\alpha_1 - \alpha_2$ occurs with lengthening of the side-groups. Fig. 24 gives corresponding experimental values of the anisotropy of the monomeric unit of the molecule $a_\parallel - a_\perp$ as a function of the number $Z = n + 2$. The points lie satisfactorily along the theoretical curve (30) (where n is replaced by Z) under the condition $S^* = 60$ (continuous line). The broken line shows the theoretical relation corresponding to $S^* = 16$, that is, under the condition that the flexibility of the side-chain equals the flexibility of a polyethylene chain.

Table 5. Number of monomeric units S in the segment, segment anisotropy $\alpha_1 - \alpha_2$, and anisotropy of the monomeric unit $a_\parallel - a_\perp$ of the molecules of some esters of poly(methacrylic acid). n is the number of carbon atoms in the alkyl side-chain of the molecule.

Polymer	n	S	$10^{25}(\alpha_1 - \alpha_2)$ cm^3	$10^{25}(a_\parallel - a_\perp)$ cm^3
Poly(methyl methacrylate)	1	7.0	−2	−0.2
Poly(butyl methacrylate)	4	6.7	−14	−2.1
Poly(hexyl methacrylate)	6	8.6	−40	−4.6
Poly(octyl methacrylate)	8	7.9	−47	−5.9
Poly(cetyl methacrylate)	16	19	−170	−8.9
Poly(phenylmethacrylic ester of cetyloxybenzoic acid)	16	26	−2500	−100

Hence the rigidity of the side-chains of poly(alkyl methacrylates), in the range n investigated (up to $n = 16$) is four times the rigidity of chain vinyl polymers of similar structure. This result shows the presence of significant orientation ordering in the side-chains of the macromolecules, considerably surpassing the conformational ordering of the ordinary gaussian chains. The reason for this ordering is evidently to be sought in the interaction of regularly constructed alkyl radicals, which leads to the formation of an intramolecular structure with a short-range orientation order in the positions of the side-chains. This effect is all the greater the longer the side-chains, just as lengthening assists the crystallisation of the polymer in bulk.

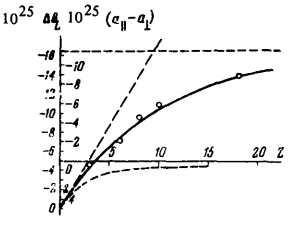


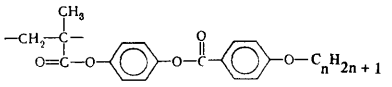
Figure 24. Variation of the anisotropy of the monomeric unit of the alkyl esters of poly(methacrylic acid) with the number of valence bonds $Z = n + 2$ in the side-chain. Continuous curve: theoretical relation according to Eqn. (30) at $\Delta a = 3.3 \times 10^{-25}$ cm^3 and $S^* = 60$. The broken curve is obtained from the equation at $\Delta a = 3.3 \times 10^{-25}$ cm^3 and $S^* = 16$.

A natural consequence of this effect is also a decrease in the flexibility of the main-chain.

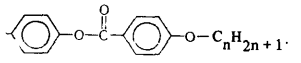
c. Polyphenyl methacrylic esters of alkyloxybenzoic acids. Convincing proof that the observable increase in the orientation order both in the main- (increase in S) and in the side- (increase in $a_\parallel - a_\perp$) chains

is the consequence of the interaction of the side-groups is given by the conformation properties of the polyphenyl methacrylic ester of alkyloxybenzoic acids (PPMEAOBA).[100]

These polymers, which have a structure of the form:



can be regarded also as esters of polymethacrylic acid where the hydrogen in the side-group is replaced by the radical:



Hence the main-chains of these macromolecules do not differ from those examined above and the lateral substituents are distinguished by the presence of groups instrumental in the formation of a liquid-crystal phase, that is, a state with a clearly expressed orientation ordering[101].

The structural characteristics of macromolecules of one of these polymers—polyphenylmethacrylic ester of cetoxybenzoic acid (PPMECOBA) ($n = 16$ in the C_nH_{2n+1} group) are given in Tables 4 and 5.

The presence of strongly interacting side-groups increases the rigidity of the main-chain of the polymer ($S = 25$). However, its optical properties are completely unique. The negative segment anisotropy of the molecule is more than an order of magnitude greater than the anisotropy of poly(cetyl methacrylate) and comparable only with the anisotropy of "crystal-like" molecules—polyisocyanate or poly-γ-benzyl-L-glutamate and the anisotropy of the monomer $a_{\parallel} - a_{\perp}$ is even appreciably greater than the anisotropy of the monomeric unit of these molecules. The last fact shows that the extremely high anisotropy of the molecule is due not so much to the rigidity of its main-chain (which is much less than for crystal-like molecules) as to the extremely perfect orientation order in its side-groups.

It is also remarkable that this order is not only axial but also polar—solutions of PPMECOBA give a high negative birefringence in an electric field. The use of these experimental results and Eqns. (18) and (24) gives a value of $\mu = 30 \times 10^{-18}$ cgse for the component of the dipole moment along the axis of the molecule. Significantly, these unique properties are combined with properties characteristic for flexible chain polymers: unlike the crystal-like molecules the dimensions of the PPMECOBA molecule are sensitive to the thermodynamic nature of the solvent and can change markedly as the latter is changed. All these facts show that in PPMECOBA molecules there is orientation ordering of a mesomorphic type, in which the side-chains of the molecule form a mobile liquid-crystalline structure.

d. Graft copolymers. Similar, although less perfect, structures are evidently formed in other macromolecules of the comblike type—graft polymers. They have quite specific optical properties, demonstrated by the example of graft polymers of styrene and alkyl methacrylates[38,102,103].

The optical anisotropy of the molecules of a graft copolymer can be many times greater than the anisotropy of the graft homopolymers. It is positive, that is, opposite in sign to the negative anisotropy of the chain of graft polystyrene, although the mass of the polystyrene in the graft copolymer exceeds 90%.

An analysis of these experimental results together with the hydrodynamic properties of the molecules [see Eqns. (11), (12), and 30)] enables the rigidity of both the main chain of the copolymer and also the chains of the graft copolymers to be determined[38]. Here the observable properties can be explained not only qualitatively but also quantitatively by the existence in the graft polymer of an intramolecular structure with a high degree of orientation order.

It is characteristic that despite the high rigidity of the main-chain of the graft polymer ($A = 100$–200 Å) the exponent in the M–K equations (5)–(7) for this polymer are close to the values $\alpha = \beta = 0.5$. This fact is explained by the high value of the diameter d of the wormlike chain, modelling the graft polymer molecule, in complete agreement with theory, Eqns. (11) and (12).

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The facts considered above show that the structural features of macromolecules leading to the appearance in them of properties characteristic for "semirigid" chains can be extremely varied (see Table 4).

Apart from the true skeletal rigidity of the single-track chain—poly(alkyl isocyanates)—additional interactions of quite different origins are possible in the molecules; however, these can be classified as "short-range actions". These interactions lead to increased rigidity of the molecular conformation. They include both purely chemical and also hydrogen bonds, leading to the formation of regular rings in the chain (staircase and partly staircase polymers, derivatives of polysaccharides, secondary helical structures of polypeptides and polynucleotides).

Furthermore, the rigidity and ordering of the conformation can be considerably increased by van der Waals interaction of the side-radicals and electrostatic repulsion of the ionogenic groups of the chain[74,105,106].

There is no doubt that the list of molecular structures which can be classified as semirigid is not limited to the examples considered above. However, in selecting the subjects for discussion we considered only those examples in which the morphological properties of the molecule have been investigated quantitatively and in sufficient detail for forming a definite opinion.

From these examples clearly the semirigid molecules cannot be regarded as a class of polymer with a definite chemical structure. This terminology should rather be applied to all the group of structures which exhibit a certain combination of physicochemical properties, which has been discussed above.

The most characteristic of these properties are a high degree of intramolecular ordering and a high value for the persistence length of the wormlike chain modelling the macromolecule.

In the range of low and moderate molecular weights these properties appear as a departure from the regularities characteristic for gaussian chains—in a specific dependence on the molecular weight of such parameters as the radius of gyration of the molecule, their optical anisotropy and dipole moments. The hydrodynamic behaviour of the semirigid chains corresponds to the conformation of a slightly bent rod.

In the range of high molecular weights the semirigid chains are already gaussian, but for these large radii of gyration, segment anisotropy (proper and microform) and dipole moments are characteristic. Considerable flow capability of the molecules is a characteristic of the hydrodynamic behaviour (when the chain diameter is not too large).

The combination of all these parameters (or some of them) can be used for the experimental observation and as a quantitative characteristic of equilibrium rigidity and the ordering of the structure of the molecular chain.

Hence we consider that the above information can be useful in two respects. Firstly, it contains various examples of those structural features of a polymer which can be responsible for its molecule having properties characteristic for semirigid chains. Secondly, it shows that the hydrodynamic, dynamo-optical, and electro-optical properties of chain molecules in solutions are reliable criteria for a quantitative appraisal of their rigidity and the internal degree of order of the structure.

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Institute of High-Molecular-Weight Compounds, Academy of Sciences of the USSR, Physical Institute, Leningrad University

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Benzoisoquinolines and Azafluorenes

N.S.Prostakov

Methods of preparation, synthetic reactions, and properties are surveyed for the difficultly accessible polyfused nitrogen-containing heterocyclic systems—benzo[*f*] isoquinoline, benzo[*g*] isoquinoline, benzo[*h*] isoquinoline, and azafluorenes in which the position of the nitrogen atom in the pyridine ring varies. A list of 77 references is included.

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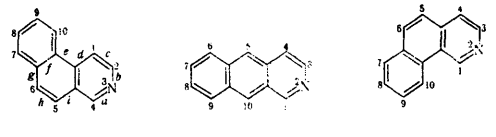
Benzoisoquinolines and azafluorenes, which are tricyclic fused nitrogen-containing systems, still remain a little studied group of compounds. An apt comparison is that the monograph "Heterocyclic Compounds"[1] devotes a long chapter to benzoquinolines, whereas only a few words are said about benzoisoquinolines and azafluorenes. Only one example is given of the synthesis of benzo[*g*]isoquinoline and the isolation of a small quantity of 9-oxo-3-phenyl-4-azafluorene-1-carboxylic acid by the oxidation of 2-phenylbenzo[*h*]quinoline-4-carboxylic acid. The information on this group of compounds to be found in the literature is also limited.

Yet both benzoisoquinolines and azafluorenes are of definite interest. Among compounds of this type have been found quite effective physiologically active substances. Their use for the synthesis of various dyes is also promising. But perhaps the greatest value of these compounds is that they can form portions of systems which closely resemble alkaloids.

I. BENZOISOQUINOLINES

The nomenclature of the benzoisoquinolines is similar to that of the benzoquinolines:



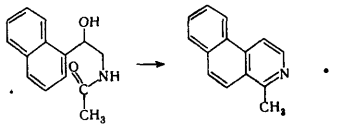
(I) (II) (III)

(I) benzo[*f*]isoquinoline (5,6-benzoisoquinoline, 2-azaphenanthrene)
(II) benzo[*g*]isoquinoline (6,7-benzoisoquinoline, 2-azaanthracene)
(III) benzo[*h*]isoquinoline (7,8-benzoisoquinoline, 3-azaphenanthrene).

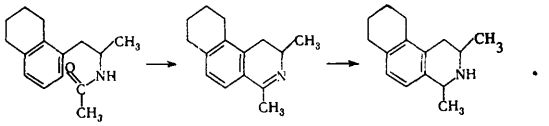
Synthetic routes for building up benzoisoquinoline systems are as yet relatively few, being limited mainly to Bischler–Napiralski[2], Pictet–Gams[3], and Pictet–Spengler[4] condensations and the dehydrocyclisation of *ortho*-substituted benzylpyridinecarboxylic acids, 4-*o*-xylylpyridines, and 4-benzyl-3-methylpyridines. The photochemical cyclisation of stilbazoles has been used in the synthesis of benzoisoquinolines.

1. Benzo[*f*]isoquinolines

4-Methylbenzo[*f*]isoquinoline can be obtained by boiling *N*-(2-hydroxy-2-naphth-1′-ylethyl)acetamide with phosphorus pentoxide in xylene[5]:

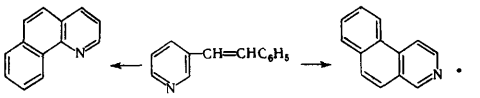


Partly hydrogenated substituted derivatives of benzo[*f*]isoquinolines have been synthesised by the Bischler–Napiralski method from *N*-[1-methyl-2-(5,6,7,8-tetrahydronaphth-1-yl)ethyl]acetamide, cyclisation being accomplished in the presence of phosphoryl chloride[6]:



1,2,7,8,9,10-Hexahydro-2,4-dimethylbenzo[*f*]isoquinoline was converted by catalytic hydrogenation into 1,2,3,4,7,8,9,10-octahydro-2,4-dimethylbenzo[*f*]isoquinoline. Several other partly hydrogenated substituted benzo[*f*]isoquinolines have been obtained by the same scheme of reactions.

The photochemical cyclisation of stilbazoles has been studied. Prolonged ultraviolet irradiation of a solution of 3-styrylpyridine and also of 3-*p*-methylstyrylpyridine in hexane yields a mixture of benzo[*f*]isoquinoline and benzo[*h*]quinoline (or the methyl derivatives of these heterocycles), which has been separated by chromatography on alumina[7,8]:

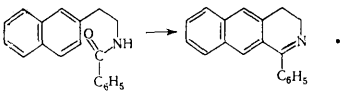


The *trans* and *cis* isomers of 3-styryl- and 3-*p*-methylstyryl-pyridines have been used in these reactions. In the same way 6-cyanobenzo[*f*]isoquinoline has been obtained from *trans*-3-β-cyanostyrylpyridine[9].

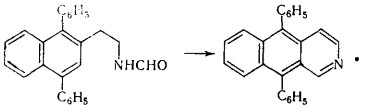
2. Benzo[*g*]isoquinolines

From the point of view of synthesis this benzoisoquinoline system has been studied in greater detail than the benzo[*f*]isoquinoline system. It can be constructed by

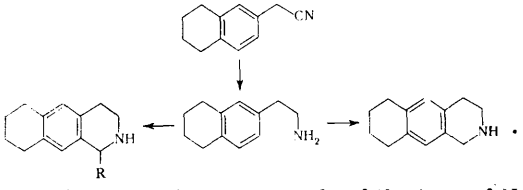
various methods. Several substituted benzo[*g*]isoquinolines have been obtained by the Bischler–Napiralski reaction. 3,4-Dihydro-1-phenylbenzo[*g*]isoquinoline has been isolated[10] by the condensation of *N*-2-naphth-2′-ylethylbenzamide (boiling in toluene with phosphoryl chloride):



3,4-Dihydrobenzoisoquinoline systems are readily converted into benzoisoquinoline systems, even by the action of atmospheric oxygen[11]. Condensation of the *N*-formyl derivative of 2-(1,4-diphenylnaphth-2-yl)ethylamine in the presence of phosphoryl bromide at once yields 5,10-diphenylbenzo[*g*]isoquinoline[12]:



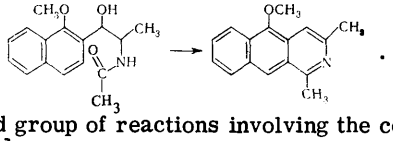
Several hydrogenated benzo[*g*]isoquinolines have been synthesised from 2-cyanomethyl-5,6,7,8-tetrahydronaphthalene[6]. On reduction with lithium tetrahydroaluminate this cyanide was converted into 2-(5,6,7,8-tetrahydronaphth-2-yl)ethylamine, which after acetylation, subsequent Bischler–Napiralski cyclisation, and hydrogenation gave 1,2,3,4,6,7,8,9-octahydro-1-methylbenzo[*g*]isoquinoline. When the same amine was condensed with formaldehyde by the Pictet–Spengler method, 1,2,3,4,6,7,8,9-octahydrobenzo[*g*]isoquinoline was isolated:



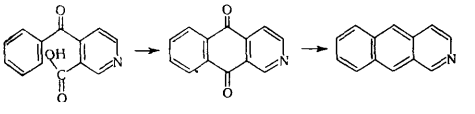
There are indications that compounds of the type of *N*-substituted 1,2,3,4,6,7,8,9-octahydro-3-methylbenzo[*g*]isoquinolines have a strong analgesic effect.

The condensation of *N*-acylated 2-(5,6,7,8-tetrahydronaphth-2-yl)-1-methylethylamines has been accomplished. 1-Benzyl-3,4,6,7,8,9-hexahydrobenzo[*g*]isoquinoline has been obtained by the cyclisation of *N*-β-(6-tetralylethyl)-phenylacetamide[13].

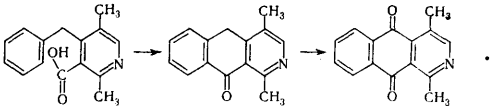
The Pictet–Gams method has been used in syntheses of benzo[*g*]isoquinolines as well as in the preparation of benzo[*f*]isoquinolines. An example is the synthesis of 5-methoxy-1,3-dimethylbenzo[*g*]isoquinoline[14]:



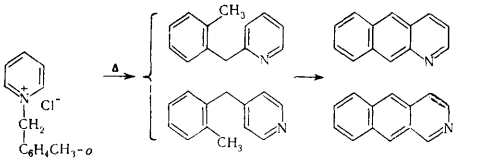
In a second group of reactions involving the construction of the benzo[*g*]isoquinoline system use is made of a preformed pyridine ring. Benzo[*g*]isoquinoline is obtained from 4-benzoylpyridine-3-carboxylic acid, which was converted by intramolecular condensation (with sulphuric acid at 175°C) into 2-aza-anthraquinone, from which benzo[*g*]-isoquinoline was obtained by reduction with zinc dust in aqueous ammonia[15]:



The cyclisation of 4-benzyl-2,5-dimethylpyridine-3-carboxylic acid by means of polyphosphoric acid yields the corresponding 2-aza-anthrone (in 85% yield), which is readily oxidised by atmospheric oxygen to 1,4-dimethyl-2-aza-anthraquinone[16]:



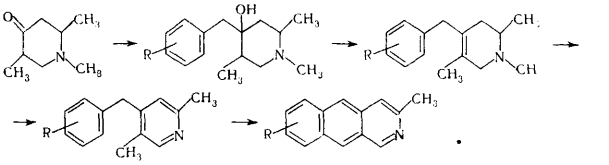
Similarly to the dehydrocyclisation of *o*-benzyltoluene to anthracene, benzo[*g*]isoquinoline has been obtained from 4-*o*-xylylpyridine. The initial substituted benzylpyridines are synthesised by Ladenburg's method, which was first developed in detail for these purposes by Chichibabin[17,18]. When *o*-xylyl chloride is heated (to 250°C) with pyridine in the presence of copper, a mixture of 2- and 4-*o*-xylylpyridine is formed, in which the latter isomer predominates. When the mixture of these substituted pyridines is passed over copper turnings or over pumice impregnated with lead oxide at 580–590°C, dehydrocyclisation takes place, with the formation of benzo[*g*]quinoline and benzo[*g*]-isoquinoline, the latter being comparatively easily isolated from the mixture because of its sparing solubility[19]:



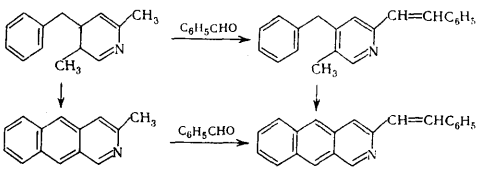
8-Methylbenzo[*g*]isoquinoline has been obtained in the same way from *o*- and *p*-dimethylbenzylpyridinium chloride.

A method has been worked out for obtaining benzo[*g*]-isoquinoline systems by the dehydrocyclisation of 4-benzyl-3-methylpyridines. The latter are synthesised from 4-oxopiperidines. The tertiary alcohols obtained from the oxopiperidines are converted by dehydration followed by catalytic dehydrogenation and *N*-dealkylation into quite high yields of substituted pyridine bases[20–22]. The dehydrocyclisation of 4-benzyl(alkylbenzyl)pyridines containing a 3-methyl group in the pyridine ring is accomplished at 500–510°C on the same dehydrogenation catalysts as are used at the stage of synthesis of 4-benzylpyridines.

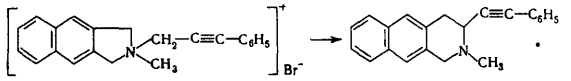
The reaction scheme given below is for the synthesis of 3-methylbenzo[*g*]isoquinoline[23] and its homologues from 1,2,5-trimethyl-4-oxopiperidine[24]:



3-Styrylbenzo[*g*]isoquinoline can be synthesised in two ways—by the direct condensation of 3-methylbenzo[*g*]isoquinoline with benzaldehyde and by the dehydrocyclisation of 4-benzyl-5-methyl-2-styrylpyridine:



The partly hydrogenated substituted derivative 1,2,3,4-tetrahydro-2-methyl-3-2′-phenylethynylbenzo[*g*]isoquinoline is formed on heating 2-(3-phenylprop-2-ynyl)benzo[*f*]-isoindolinium bromide in the presence of anhydrous caustic soda in benzene, the starting material being obtained from 2-methylbenzo[*f*]isoindoline and 3-phenylprop-2-ynyl bromide. These transformations are based on the rearrangement of derivatives of prop-2-ynylammonium halides:



The structure of the heterocyclic compound obtained was proved by means of its ultraviolet and nuclear magnetic resonance spectra[25].

Benzo[*g*]isoquinoline[3] are high-melting, usually sparingly soluble substances, which sublime in a high vacuum. In some solvents they fluoresce. They resemble anthracene in electronic structure. Their ultraviolet spectra are very alike[12,26,27]. Benzo[*g*]isoquinolines, like anthracene, exhibit two systems of absorption bands—a Y-band (2500 Å), due to vibrations of π-electrons in the plane of the rings, and an X-band (3000–3500 Å), due to vibrations of excited π-electrons perpendicular to the plane of the rings.

Comparison of the ultraviolet spectra of unsubstituted benzo[*g*]quinoline and benzo[*g*]isoquinoline with that of anthracene reveals a slight (10 Å or 140 cm^{-1}) bathochromic shift in the Y-band in the former, and a slight (20 Å or 350 cm^{-1}) hypsochromic shift in the same band in the latter. The X-system of bands exhibits a bathochromic displacement of the long-wavelength boundary of the region by 90 and 160 Å (625 and 1000 cm^{-1}) respectively in benzo[*g*]-quinoline and benzo[*g*]isoquinoline, and a decrease in intensity of absorption in the X-region (by a factor of about 1.5).

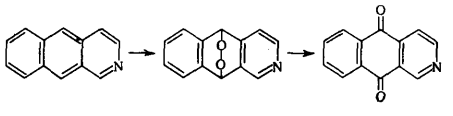
The effect of the nitrogen atom in these systems is analogous to that of such non-chromophoric substituents in the anthracene molecule as chloro and alkyl.

meso-Disubstituted benzo[*g*]isoquinolines show an additional absorption peak in the region of 3000 Å. It is assumed[26] that the pyridine ring, and also phenyl rings in *meso*-positions in substituted benzo[*g*]isoquinolines, do not lie in the plane of the naphthalene ring system.

Several papers present results of quantum-mechanical calculations on benzo[*g*]isoquinoline systems[28–32].

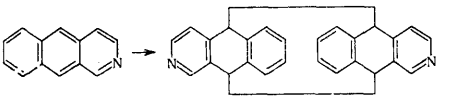
Benzo[*g*]isoquinoline forms an adduct with maleimide[12].

Like aromatic linear fused tricyclic systems, benzo[*g*]-isoquinolines undergo photochemical reactions[33,34]. When a solution of benzo[*g*]isoquinoline in carbon disulphide is exposed to sunlight, an unstable photo-oxide is formed, which is oxidised in the air to 2-aza-anthraquinone (3,4-phthaloylpyridine):



Exposure of a solution of 5,10-diphenylbenzo[*g*]isoquinoline in carbon disulphide gave a 20% yield of its photo-oxide (colourless), and this decomposes at 145–165°C, evolving up to 80% of the combined oxygen[12,35].

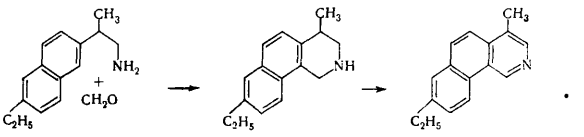
As with anthracene, illumination of solutions of benzo-[*g*]isoquinoline in alcohol, acetone, benzene, or ether in the absence of air yields greenish crystals of a "photo-dimer", which does not melt, but on being heated regenerates the monomer[34]:



The ultraviolet spectrum of the "photodimer" contains maxima characteristic of pyridine and benzene, the reason for this being the "disengagement" of these rings.

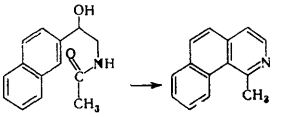
3. Benzo[*h*]isoquinolines

The usual methods for building up isoquinoline systems are employed in the synthesis of benzo[*h*]isoquinolines. Application of the Pictet–Spengler method for the condensation of 2-(6-ethylnaphth-2-yl)propylamine with formaldehyde gives 8-ethyl-1,2,3,4-tetrahydro-4-methylbenzo[*h*]isoquinoline, which on dehydrogenation by means of selenium (at 340°C) is converted into 8-ethyl-4-methylbenzo[*h*]isoquinoline[36]:

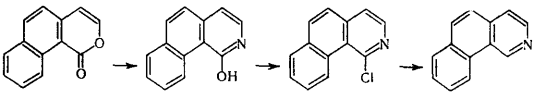


1,2,3,4-Tetrahydrobenzo[*h*]isoquinoline has been synthesised by the same method—by condensing 2-naphth-2′-ylethylamine with formaldehyde[37].

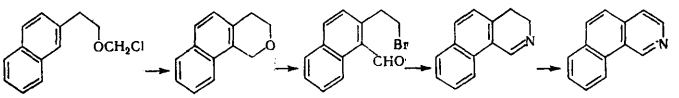
The Pictet–Gams method has been used to obtain 1-methylbenzo[*h*]isoquinoline from *N*-(2-hydroxy-2-naphth-2′-ylethyl)acetamide[38]:



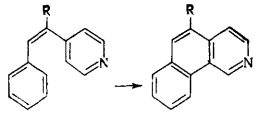
Several preparations of benzo[*h*]isoquinolines start from oxygen-containing fused tricyclic heterocycles. When 7,8-benzoisocoumarin is heated with an alcoholic solution of ammonia, 1-hydroxybenzo[*h*]isoquinoline is formed. Replacement of the hydroxyl by chlorine and subsequent removal of the latter by hydrogenation (palladium on charcoal, alcoholic caustic soda solution) converted it into benzo[*h*]isoquinoline[38]:



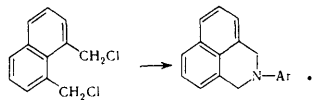
2-2′-Chloromethoxyethylnaphthalene on treatment with aluminium chloride in carbon disulphide is converted into 7,8-benzoisochroman, subsequent bromination of which with cleavage of the oxygen ring leads to 2-2′-bromoethyl-naphthal-1-aldehyde. Heating this δ-halogenated aldehyde with ammonia, by the well known method used in the synthesis of isoquinolines[39], gave 3,4-dihydrobenzo[*h*]isoquinoline, which on dehydrogenation over platinum black was converted into benzo[*h*]isoquinoline[40]:



Benzo[*h*]isoquinolines are formed by the photocyclisation of γ-stilbazoles. *trans*-4-Styrylpyridine and *trans*-4-α-methylstyrylpyridine yield respectively benzo[*h*]isoquinoline and 5-methylbenzo[*h*]isoquinoline[9]:

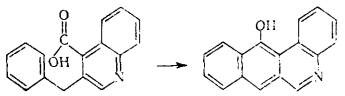


The synthesis of a partly hydrogenated benzo[*de*]isoquinoline system has been described. Several 2-aryl-2,3-dihydro-1*H*-benzo[*de*]isoquinolines have been obtained from 1,8-bischloromethylnaphthalene and primary amines in the presence of triethylamine (boiling in toluene):



Compounds of this type do not form peroxy-compounds when treated in chloroform or benzene solution with oxygen in the light at 60°C.[41]

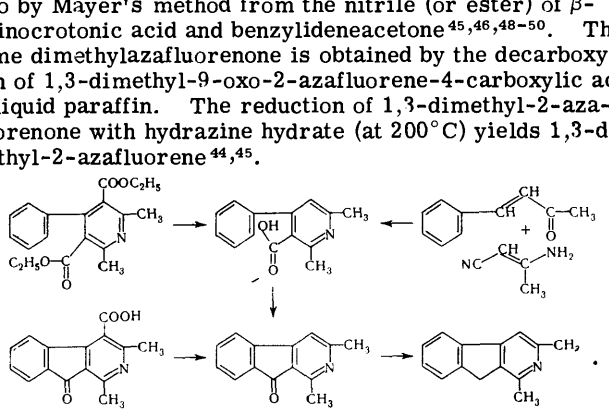
Information on the synthesis of dibenzoisoquinolines is extremely limited. An example is 5-hydroxy-3,4:6,7-dibenzoisoquinoline, which is obtained by the intramolecular condensation of 3-benzylcinchoninic acid in the presence of aluminium chloride:



Similarly 5-hydroxy-1-phenyl-3,4:6,7-dibenzoisoquinoline has been synthesised from 3-benzyl-2-phenylcinchoninic acid (obtained from ω-benzylacetophenone and isatinic acid)[42,43].

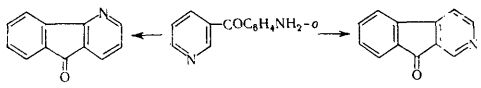
II. AZAFLUORENES

Among this group of compounds the 2-azafluorenes have been the most thoroughly studied. A usual method of synthesising 2-azafluorenes and their derivatives consists in the cyclisation of substituted pyridinecarboxylic acids. 1,3-Dimethyl-2-azafluorenone is obtained in ~90% yield from 2,6-dimethyl-4-phenylpyridine-3-carboxylic acid (by heating with sulphuric acid at 100°C) and in lower yield from the chloride of this acid (by treatment with aluminium chloride)[44-46]. The initial 2,6-dimethyl-4-phenylpyridine-3-carboxylic acid is obtained by the partial hydrolysis of diethyl 2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate with subsequent decarboxylation of the 5-ethoxycarbonyl-2,6-dimethyl-4-phenylpyridine-3-carboxylic acid[47], and also by Mayer's method from the nitrile (or ester) of β-aminocrotonic acid and benzylideneacetone[45,46,48-50]. The same dimethylazafluorenone is obtained by the decarboxylation of 1,3-dimethyl-9-oxo-2-azafluorene-4-carboxylic acid in liquid paraffin. The reduction of 1,3-dimethyl-2-azafluorenone with hydrazine hydrate (at 200°C) yields 1,3-dimethyl-2-azafluorene[44,45].



Dehydrocyclisation of the appropriate substituted pyridine-3-carboxylic acids yields 9-oxo-2-azafluorene-1-carboxylic acid and 7-methoxy(or hydroxy)-1,3-dimethyl-2-azafluorenone[44,51,52]. 2-Azafluorene itself (pyridofluorene) can be isolated by the decarboxylation of 2-azafluorene-1,3,4-tricarboxylic acid in the presence of soda-lime[51]. Condensation with conversion to the corresponding 2-azafluorenone could not be achieved with 2,6-dimethyl-4-*p*(or *m*)-nitrophenylpyridine-3-carboxylic acid. The condensation of 4-*o*-methoxyphenyl-2,6-dimethylpyridine-3-carboxylic acid yields 9,10-dihydro-1,3-dimethyl-10-oxo-9-oxa-2-azaphenanthrene[44,51,52].

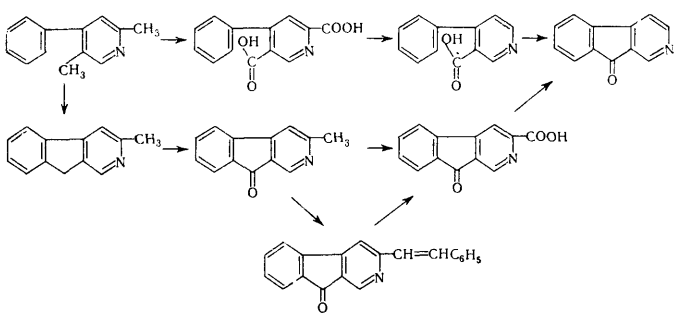
The cyclisation of 3-*o*-aminobenzoylpyridine has been accomplished in investigations of the mechanism of the Pschorr reaction. Ultraviolet irradiation in acid solution was used, the products being 2-azafluorenone (26.2%) and 4-azafluorenone (36.8%)[53]:



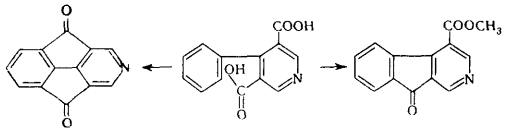
3-Mesitoyl(or duroyl)pyridine reacts with phenylmagnesium bromide to form compounds corresponding to dihydrophenylated 3-mesitoyl(or duroyl)pyridine. On dehydrogenation they yield 3-mesitoyl(or duroyl)-4-phenylpyridine, which when heated (185–200°C at 25 mm) is converted into 2-azafluorenone in 50% yield[54].

4-Aryldimethylpyridines have also been used in the synthesis of substituted 2-azafluorenes. Such systems can be obtained in two ways from 2,5-dimethyl-4-phenylpyridine. Oxidation of the pyridine base and partial decarboxylation of the resulting 4-phenylpyridine-2,5-dicarboxylic acid led to the preparation of 4-phenylpyridine-3-carboxylic acid, cyclisation of which yielded 2-azafluorenone[23].

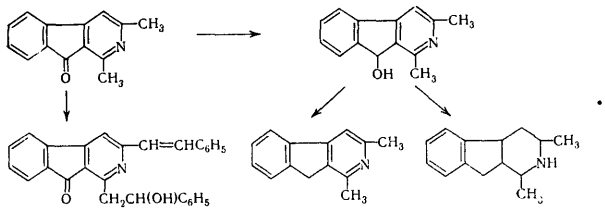
The second route consists in the dehydrocyclisation of 4-aryl-2,5-dimethylpyridines on dehydrogenation catalysts at 500–520°C. The 3-methyl-2-azafluorene obtained from 2,5-dimethyl-4-phenylpyridine in this way was converted into 3-methyl-2-azafluorenone, into 9-oxo-2-azafluorene-3-carboxylic acid, and into 2-azafluorenone[55]:



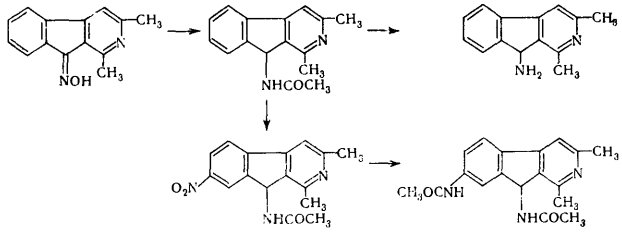
The dehydrocyclisation of 2,5-dimethyl-4-*p*-tolylpyridine yields 3,7-dimethyl-2-azafluorene, which has been converted into 3,7-dimethyl-2-azafluorenone[56]. When 4-phenylpyridine-3,5-dicarboxylic acid undergoes dehydrocyclisation, methyl 9-oxo-2-azafluorene-4-carboxylate is obtained together with a small quantity of 3-azatetracyclo-[9,2,1,$0^{5,13}$,$0^{7,12}$]tetradeca-2,4,7,9,11,13-hexaene-6,14-dione[57]:



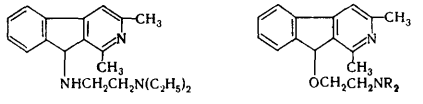
There are indications that derivatives of 1,3-dimethyl-2-azafluorene exert a spasmolytic action. 1,3-Dimethyl-2-azafluorenone has been subjected to several chemical transformations in order to obtain physiologically active substances. Its reduction with zinc dust in an aqueous-alcoholic solution of ammonia gave 1,3-dimethyl-2-azafluorenol (identified as the picrate), which on further reduction with sodium in alcohol was converted into hexahydro-1,3-dimethyl-2-azafluorene and 1,3-dimethyl-2-azafluorene. Condensation of 1,3-dimethyl-2-azafluorenone with benzaldehyde in the presence of zinc chloride gives 1-2′-hydroxyphenethyl-3-styryl-2-azafluorenone:



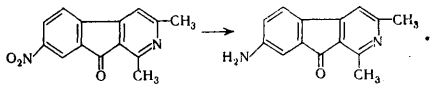
1,3-Dimethyl-2-azafluorenone oxime is reduced by zinc dust in acetic acid or anhydride to 1,3-dimethyl-2-azafluorene and 9-acetamido-1,3-dimethyl-2-azafluorene. The latter could be hydrolysed by treatment with phosphoric acid at 200°C. The resulting 9-amino-1,3-dimethyl-2-azafluorene is a strong base, which actively absorbs carbon dioxide from the air. 9-Acetamido-1,3-dimethyl-2-azafluorene can be nitrated, the nitro-derivative obtained in quantitative yield being assumed to have the structure 9-acetamido-1,3-dimethyl-7-nitro-2-azafluorene. Reduction of this product with zinc dust in acetic anhydride yields (presumably) 7,9-diacetamido-1,3-dimethyl-2-azafluorene[44,51].



9-2′-Diethylaminoethylamino-1,3-dimethyl-2-azafluorene, obtained from 9-amino-1,3-dimethyl-2-azafluorene and 2-diethylaminoethyl chloride, is similar in structure to Antergan[58]. Other derivatives of 2-azafluorene, the 9-2′-dialkylaminoethoxy-1,3-dimethyl-2-azafluorenes, resemble Dimedrol, and have been prepared from 1,3-dimethyl-2-azafluorenol and the corresponding dialkylaminoethyl chlorides (by heating with sodamide in benzene):



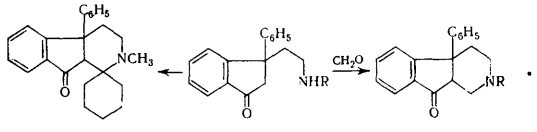
The nitration of 9-acetamidofluorene with fuming nitric acid yields two nitro-derivatives—9-acetamido-2,7(and 2,5)-dinitrofluorenes—which have been oxidised to the corresponding dinitrofluorenones[59]. The nitration of 1,3-dimethyl-2-azafluorenone gives a good yield of a mononitro-derivative, which by analogy with the nitro-derivative formed by the nitration of fluorenone itself under similar conditions, is assumed to be 1,3-dimethyl-7-nitro-2-azafluorenone. This nitro-derivative is reduced to 7-amino-1,3-dimethyl-2-azafluorenone, in which the amino-group exhibits an imino-character[48]:



The isomeric 4-amino-1,3-dimethyl-2-azafluorenone is obtained by Hofmann's reaction from 4-carbamoyl-1,3-dimethyl-2-azafluorenone. It did not prove possible to effect the conversion from ethyl 5-amino-2,6-dimethyl-4-phenylpyridine-3-carboxylate, through the 5-diacetylamino- and 5-benzamido-2,6-dimethyl-4-phenylpyridine-3-carboxylic acid (cyclisation in the presence of sulphuric acid), to a 4-amino-1,3-dimethyl-2-azafluorenone substituted in the amino-group[48].

When 3-benzoyl-1,2,5,6-tetrahydro-1-methyl-4-phenylpyridine is treated with hydrazine hydrate in the presence of sodium methoxide (in triethylene glycol at 190°C), 3-benzyl-1,2,5,6-tetrahydro-1-methyl-4-phenylpyridine is formed, and in the form of its hydrochloride has been subjected to cyclisation (with polyphosphoric acid at 130°C). Chromatographic separation of the reaction products on aluminium oxide led to the isolation of a partly hydrogenated substituted 2-azafluorene—racemic 1,2,3,4,4a,9a-hexahydro-2-methyl-4a-phenyl-4*H*-indeno[2,1-*c*]pyridine.

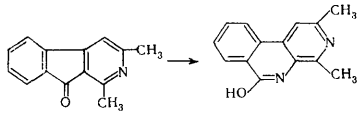
Analogous partly hydrogenated 2-azafluorene systems have been obtained by the Wolff–Kishner reduction of 1,2,3,4,4a,9a-hexahydro-6-methoxy-2-methyl-9-oxo-4a-phenylindeno[2,1-*c*]pyridine and by reducing 1,2,3,4,4a,9a-hexahydro-9-oxo-4a-phenyl-2-propyl(or cyclopropyl)-indeno[2,1-*c*]pyridine with zinc. In one of the procedures the initial oxo-derivatives are obtained by condensing *N*-methyl(propyl, or cyclopropyl)-2-(3-oxo-1-phenylindan-1-yl)ethylamine with formaldehyde in acid medium:



When a mixture of *N*-methyl-2-(3-oxo-1-phenylindan-1-yl)-ethylamine and cyclohexanone is treated with aluminium isopropoxide in toluene, spirocyclohexane-1,1′-1,2,3,4,4a,9a-hexahydro-2-methyl-9-oxo-4a-phenylindeno[2,1-*c*]pyridine is obtained, and the spirocycloheptane analogue is obtained in the same way[60].

Among compounds containing a partly hydrogenated 2-azafluorene system, 2,3,4,9-tetrahydro-2-methyl-9-phenyl-1*H*-indeno[2,1-*c*]pyridine (Phenindamine, Tephorin) has been proposed as an antihistamine preparation[61].

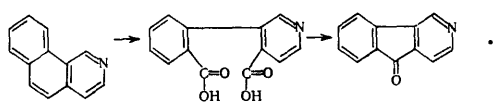
The possibility has been studied of passing from the 2-azafluorene to the diazaphenanthrene system. Beckmann expansion of the ring, with 1,3-dimethyl-2-azafluorenone oxime as starting material, could not be accomplished. Application of the Schmidt reaction to the ketone gave 9-hydroxy-1,3-dimethyl-2,10-diazaphenanthrene, the structure of which was proved by comparison with the analogous substance formed by the oxidation of 1,3,9-trimethyl-2,10-diazaphenanthrene with chromic acid[48]:



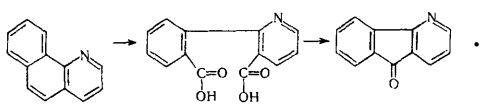
Ethyl 1,3-dimethyl-9-oxo-2-azafluorene-4-carboxylate has been converted by the Schmidt rearrangement into a

35% yield of ethyl 9-hydroxy-1,3-dimethyl-2,10-diazaphenanthrene-4-carboxylate, some of whose reactions and whose structure have been studied.

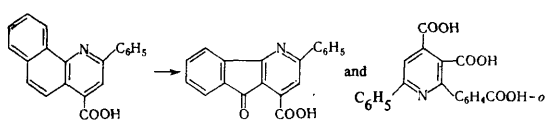
There are indications that compounds of the 3-azafluorene series possess sedative, neuroleptic, and adrenolytic activity[62]. However, very little work has been done on 3- and 4-azafluorenes. Benzo[*h*]isoquinoline has been used to obtain 3-azafluorenone itself. 3-Phenylpyridine-4,*o*-dicarboxylic acid was isolated from its oxidation, and thermal condensation of this compound led to 3-azafluorenone[38]:



4-Azafluorenone has been obtained in a similar way from 2-phenylpyridine-3,*o*-dicarboxylic acid, which was isolated from the oxidation of benzo[*h*]quinoline:

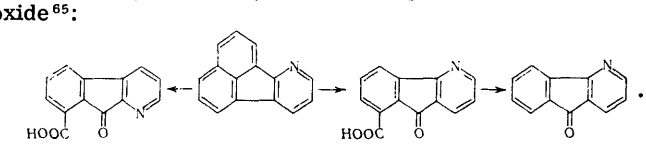


A small quantity of 9-oxo-3-phenyl-4-azafluorene-1-carboxylic acid is formed together with 2,6-diphenylpyridine-3,4,*o*(2)-tricarboxylic acid by the oxidation of 2-phenylbenzo[*h*]quinoline-4-carboxylic acid[63]:

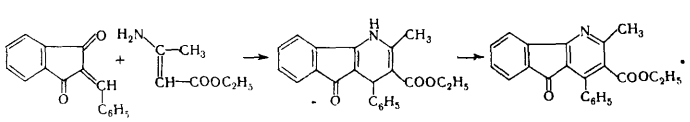


In a similar manner 9-oxo-4-azafluorene-1,3-dicarboxylic acid has been obtained from benzo[*h*]quinoline-2,4-dicarboxylic acid, and 9-oxo-1-azafluorene-2,4-dicarboxylic acid from benzo[*f*]quinoline-1,3-dicarboxylic acid[64].

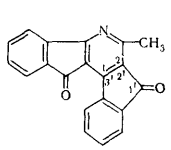
The oxidation with potassium permanganate of 10-azafluoranthene, isolated by the fractional distillation of coal-tar pitch, yields a mixture of 9-oxo-1(and 4)-azafluorene-8-carboxylic acids, from the latter of which 4-azafluorenone is obtained by decarboxylation in the presence of calcium oxide[65]:



Condensation of 2-benzylideneindane-1,3-dione with ethyl β-aminocrotonate produces ethyl 1,4-dihydro-3-methyl-9-oxo-1-phenyl-4-azafluorene-2-carboxylate, which after oxidation with chromic acid in acetic acid is converted into ethyl 3-methyl-9-oxo-1-phenyl-4-azafluorene-2-carboxylate:



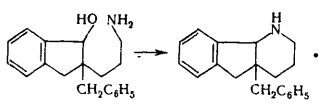
Hydrolysis of this ester (by heating it with concentrated sulphuric acid) leads to further condensation, with the formation of 3-methyl-4-azaindeno(3′,2′ : 1,2)fluorene-1′,9-dione



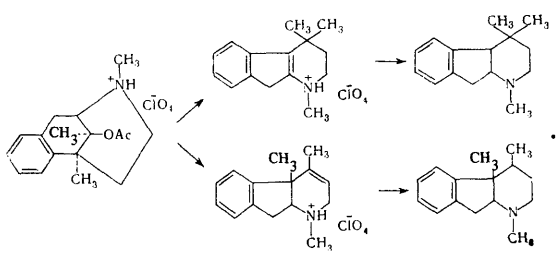
Various substituted 1-aryl-4-azafluorenones have been obtained by the method used to synthesise ethyl 3-methyl-9-oxo-1-phenyl-4-azafluorene-2-carboxylate. The oxime of this ester has been converted into the 9-diacetylamino- and 9-acetamido-derivatives[66]. 2-Aminopropenyl methyl and phenyl ketones and β-aminocinnamonitrile have also been used for condensation with benzylideneindane-1,3-dione, the products being respectively 2-acetyl- and 2-benzoyl-3-methyl-1-phenyl-4-azafluorenones and 2-cyano-1,3-diphenyl-4-azafluorenone. An attempt to prepare 1-alkyl-4-azafluorenones in a similar manner was unsuccessful.

α-(1,3-Dioxoindan-2-yl)benzylmalonamide has been cyclised to 1,2,4-trihydro-3,9-dioxo-1-phenyl-4-azafluorene-2-carboxyamide, from which saponification followed by decarboxylation yielded 1,2,3,4-tetrahydro-1-phenyl-4-azafluorene-3,9-dione[67].

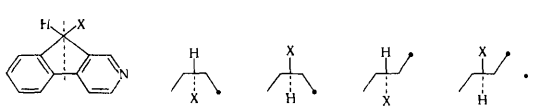
A partly hydrogenated substituted 4-azafluorene system, 4a-benzyl-1,2,3,4-tetrahydro-5*H*-indeno[1,2-*b*]pyridine, has been isolated by the condensation of 2-2′-aminopropyl-2-benzylindan-1-ol, this being obtained by the hydrogenation of 2-benzyl-2-2′-cyanoethylindan-1-one:



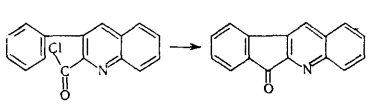
Information on the preparation of 1-azafluorene derivatives is extremely sparse. A partly hydrogenated substituted 1-azafluorene is obtained by the pyrolysis of the perchlorate of 9-acetoxy-2,5,9-trimethyl-6,7-benzomorphan. The perchlorates of 1,2,3,4-tetrahydro-1,4,4-trimethyl-9*H*-indeno[2,1-*b*]pyridine and 1,2,4a,9a-tetrahydro-1,4,4a-trimethyl-9*H*-indeno[2,1-*b*]pyridine were isolated, and were then hydrogenated in the nitrogen-containing ring[68,69]:



Papers on the stereochemistry of substituted azafluorenes are almost completely lacking. It has been suggested[52] that 9-substituted azafluorenes may have four geometrical isomers owing to a non-planar structure:

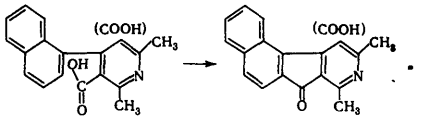


Intramolecular cyclisation is the principal method employed in the synthesis of azabenzofluorene structures. Application of the Friedel–Crafts reaction to 3-phenylquinoline-2-carbonyl chloride (in nitrobenzene) yields 1-aza-2,3-benzofluorenone[70]:

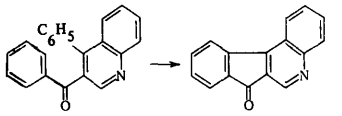


1,3-Dimethyl-2-aza-5,6-benzofluorenone has been obtained from 2,6-dimethyl-4-naphth-1′-ylpyridine-3-carbonyl

chloride and also from 2,6-dimethyl-4-naphth-1′-ylpyridine-3,5-dicarboxylic acid, 1,3-dimethyl-9-oxo-2-aza-5,6-benzofluorene-4-carboxylic acid also being isolated in the latter case[44]:

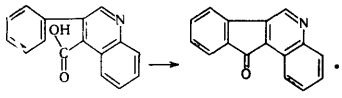


3-Benzoyl-4-phenylquinoline and also 3-mesitoyl-4-phenylquinoline are cyclised under the influence of polyphosphoric acid to 2-aza-3,4-benzofluorenone[54]:

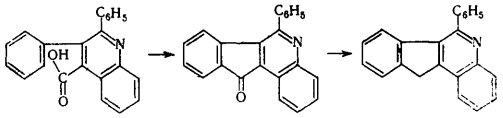


The same azafluorenone is obtained by the cyclisation of 4-phenylquinoline-3-carboxylic acid[71].

3-Aza-1,2-benzofluorenone can be synthesised by the condensation of 3-phenylcinchoninic acid by means of sulphuric acid[70]:

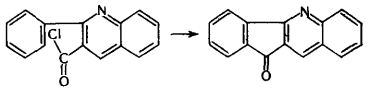


Analogous 4-alkylated (or 4-phenylated) azabenzofluorenones are obtained from 2-substituted 3-phenylcinchoninoyl chlorides by the Friedel–Crafts reaction and also from the acids themselves[43,71]. An example is the synthesis of 4-phenyl-3-aza-1,2-benzofluorenone from 2,3-diphenylcinchoninic acid:

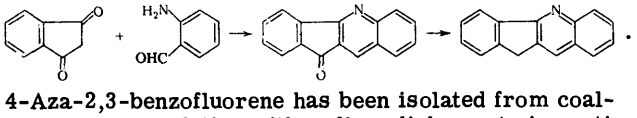


Conversion to azafluorene structures is accomplished by means of hydrazine hydrate or by reduction with tin in a mixture of acetic and hydrochloric acids.

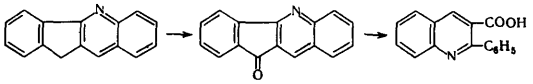
2-Phenylquinoline-3-carboxylic acid and also its chlorides are used in the synthesis of 4-aza-2,3-benzofluorenone[71]:



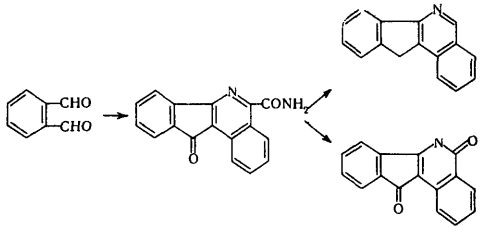
4-Aza-2,3-benzofluorenone is also obtained by condensing *o*-aminobenzaldehyde with indane-1,3-dione, and is then reduced with zinc dust to 4-aza-2,3-benzofluorene[72]:



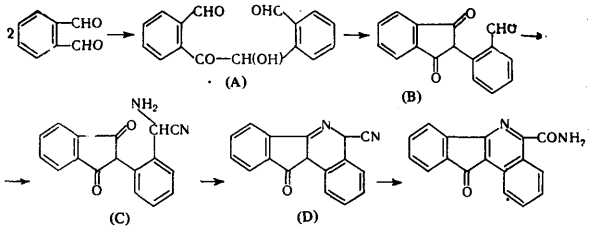
4-Aza-2,3-benzofluorene has been isolated from coal-tar pitch. Its oxidation with sodium dichromate in acetic acid yielded 4-aza-2,3-benzofluorenone. In molten caustic potash the latter is converted into 2-phenylquinoline-3-carboxylic acid[65]:



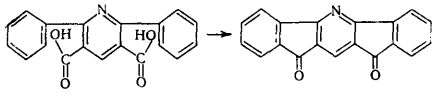
Treatment of phthalaldehyde with sodium cyanide gives a low yield of 9-oxo-4-aza-1,2-benzofluorene-3-carboxyamide. Hydrolysis of the latter with hydrochloric acid, followed by reduction with zinc in acetic acid, led to 4-aza-1,2-benzofluorene, oxidation of which with copper sulphate in pyridine yielded 11-oxoindeno[1,2-*c*]isocarbostyryl[73]:



The mechanism suggested for this reaction is that treatment of phthalaldehyde with sodium cyanide involves initially a normal benzoin condensation (A). Intramolecular condensation then yields an indanedione structure (B), the free aldehyde group of which is attacked by cyanide and ammonia with conversion into an amino-nitrile grouping (C). This latter undergoes cyclisation with formation of the dihydroisoquinoline system (D). On oxidation with atmospheric oxygen hydrolysis takes place, with formation of the final product—9-oxo-4-aza-2,3-benzofluorene-3-carboxyamide (1-carbamoyl-11-oxoindeno[1,2-*c*]isoquinoline).

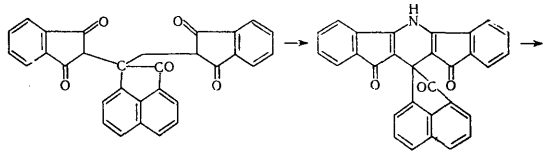


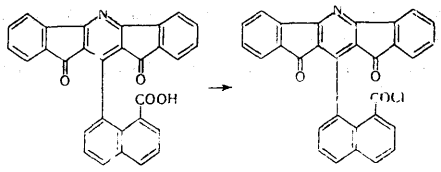
Pentacyclic fused ring systems containing nitrogen, belonging to azafluorene systems, have been obtained by the intramolecular condensation (double cyclisation) of diphenylated 3,5-dicarboxylic acids. Thus 2,6-diphenylpyridine-3,5-dicarboxylic acid yields 2,3 : 5,6-dibenzoylenepyridine[45]:



Similarly, 6-methyl-2,3 : 4,5-dibenzoylenepyridine has been synthesised from 6-methyl-2,4-diphenylpyridine-3,5-dicarboxylic acid[49,66].

An azafluorene compound of this type is a preparation termed Dibepyne, which is 8-(2,3(CO) : 6,5(CO)-dibenzoylenepyrid-4-yl)naphth-1-oyl chloride. Dibepyne is an analytical reagent for primary amines. The starting material in its synthesis is 2,2-di-indanedionylacenaphthen-1-one. When this interacts with ammonium acetate the nitrogen-containing ring closes, with the formation of acenaphthen-1-onespiro(2,4′)-2′,3′(CO) : 6′,5′(CO)-dibenzoylene-1′,4′-dihydropyridine. Subsequent treatment of this compound with hydrogen peroxide, followed by thionyl chloride, leads to the formation of Dibepyne[74–76]:





Several compounds have been synthesised which are analogous in structure to Dibepyne[77].

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Department of Organic Chemistry,
Lumumba University of International
Friendship, Moscow

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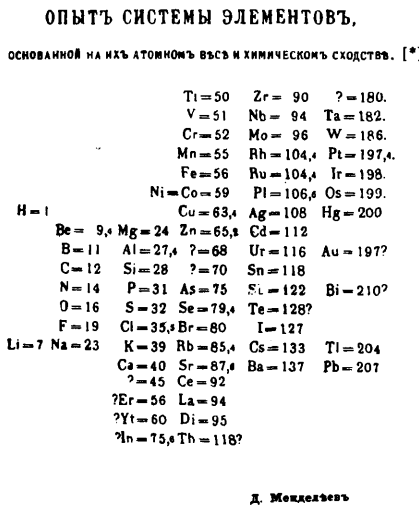
A Century of Mendeleev's Periodic Law

V.I.Spitsyn

At the beginning of March 1869 D.I. Mendeleev, Professor of Chemistry at the University of St. Petersburg, distributed among many Russian and foreign scientists sheets which depicted the system of the elements which he had worked out on the basis of their atomic weights and chemical similarity (Fig. 1).



ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ,

ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВѢСѢ И ХИМИЧЕСКОМЪ СХОДСТВѢ. [*]

			Ti=50	Zr= 90	?=180.	
			V=51	Nb= 94	Ta=182.	
			Cr=52	Mo= 96	W=186.	
			Mn=55	Rh=104,4	Pt=197,4.	
			Fe=56	Ru=104,4	Ir=198.	
			Ni=Co=59	Pl=106,6	Os=199.	
H=1			Cu=63,4	Ag=108	Hg=200	
	Be= 9,4	Mg=24	Zn=65,2	Cd=112		
	B=11	Al=27,4	?=68	Ur=116	Au=197?	
	C=12	Si=28	?=70	Sn=118		
	N=14	P=31	As=75	Sb=122	Bi=210?	
	O=16	S=32	Se=79,4	Te=128?		
	F=19	Cl=35,5	Br=80	I=127		
Li=7	Na=23	K=39	Rb=85,4	Cs=133	Tl=204	
		Ca=40	Sr=87,6	Ba=137	Pb=207	
		?=45	Ce=92			
		?Er=56	La=94			
		?Yt=60	Di=95			
		?In=75,6	Th=118?			

Д. Менделѣевъ

Figure 1. First representation of D.I. Mendeleev's Periodic System of the elements (1869).

* Trial system of the elements based on their atomic weight and chemical similarity.

A lecture on this work by Mendeleev was given at a meeting of the Russian Chemical Society held on 18th March 1869, and in May of the same year his paper "Relationship between the Properties of Elements and their Atomic Weights" was published in the next issue of the Journal of the Russian Chemical Society[1]. This contained the first formulation of the Periodic Law: "The elements, when arranged in the order of their atomic weights, exhibit a clear periodicity of properties". A few years later Mendeleev gave a still more precise formulation of the Periodic Law: "The properties of the elements, as well as the structure and the properties of their compounds, vary periodically with the atomic weights of the elements".

The discovery of the Periodic Law and the associated natural system of the chemical elements was a consequence of Mendeleev's work on "The Principles of Chemistry", his famous textbook of inorganic chemistry, which he began to write in 1868. "It contains many original ideas..., the chief of which is the periodicity of the elements, which was actually discovered in working on 'The Principles of Chemistry'", as Mendeleev subsequently pointed out[2].

It is well known that attempts to classify the elements—to arrange them into groups and tables—had been made even before Mendeleev's time. Mention may be made of Döbereiner's triads (1829)—calcium, strontium, barium; sulphur, selenium, tellurium; etc.—which developed into Pettenkofer's groups (1850)—nitrogen, phosphorus, arsenic, antimony; magnesium, calcium, strontium, barium; etc.—Chancourtois's spiral (1862), the tables of Odling (1864) and Meyer (1864), and Newlands' octaves (1866). However, these works were devoted either to particular isolated questions of the similarity of groups of elements

Ряды	Группа I — R^2O	Группа II — RO	Группа III — R^2O^3	Группа IV RH^4 RO^2	Группа V RH^3 R^2O^5	Группа VI RH^2 RO^3	Группа VII RH R^2O^7	Группа VIII — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59; Cu=63
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=97	—=100	Ru=107, Rh=104, Pd=106, Ag=108
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199
11	(Au=199)	Hg=200	Te=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=251	—	U=240	—	— — — —

Figure 2. Mendeleev's Periodic System of the elements (1872).

or to the search for relations between their atomic weights. None of these authors sought general relations between the properties of all known chemical elements; no-one before Mendeleev had formulated the Periodic Law.

It must be remarked that Mendeleev, although he stressed his view that "the value of the atomic weight determines the character of the element", considered that other characteristics of the chemical elements were also of fundamental importance. The chemical properties of the compounds formed were no less significant for determining the position of elements in the Periodic System. In some cases—cobalt and nickel, tellurium and iodine—the sequence of increasing atomic weight was disregarded in Mendeleev's table.

The outstanding scientific and philosophical value of Mendeleev's discovery consisted primarily in the establishment of an interrelationship between all the chemical elements, their physical and chemical properties. Groups and series in the Periodic System became a reliable basis for revealing families of related elements.

The first practical application of the Periodic Law was to correct the valencies and the atomic weights of certain elements, for which incorrect values had hitherto been accepted. This applied in particular to indium, cerium and other rare-earth metals, thorium, and uranium. Indium had been regarded as a bivalent element, and on the basis of its atomic weight (75.6)† was located between arsenic and selenium, although clearly not resembling them in properties. Measurement of the heat capacity of metallic indium, together with a detailed examination of the properties of its compounds, led Mendeleev to the conclusion that indium must be regarded as tervalent in its higher state of oxidation. Its atomic weight then became 113, and indium found a place in Group III of the Periodic System between cadmium (112) and tin (118), in full agreement with its chemical properties. However, this position had originally been occupied by uranium, which had been assumed to be a tervalent element having an atomic weight of 116. Mendeleev soon came to the conclusion that uranium was closer to molybdenum and tungsten than to aluminium in chemical properties, doubled the atomic weight of uranium, and placed it in Group VI of the Periodic System.

Mendeleev adduced similar considerations to justify the tervalency of the ceritic elements (lanthanum, etc.), which many chemists regarded as bivalent. He assigned the formula CeO_2 to the higher oxide of cerium, and ThO_2 (instead of ThO) to that of thorium. Hence new values were calculated for the atomic weights of these elements.

This work, of course, was by no means easy. It must be remembered that no methods were then available for measuring directly the atomic weights of elements; only Dulong and Petit's law of atomic heats gave some assistance in this direction. The great expert on the chemistry of the rare-earth metals K. Rammelsberg objected to Mendeleev's proposed changes in the atomic weights of cerium, didymium, and lanthanum, while Lothar Meyer considered that in general "it would be rash to alter the hitherto accepted atomic weights on such an unreliable basis", by which he meant the Periodic Law.

Mendeleev's view that the atomic weights of the platinum metals should be corrected so that they would increase—not diminish—in the sequence osmium–iridium–platinum (as followed from old analytical results) was soon confirmed. However, his suggestion that the atomic weight of tellurium should be lower than that of iodine was not justified, the reason for this depending, as we now know, on the nature of the isotopes of these two elements, not on the chemical properties of their atoms. In spite of the apparent inconsistency with the main rule on which the Periodic System was constructed—the arrangement of the elements in order of increasing atomic weight—Mendeleev left tellurium in Group VI, and iodine in Group VII, on the basis of their valency and chemical properties.

Thus as a result of intense creative work, overcoming immense difficulties, Mendeleev produced within a short time (less than two years) essentially the same Periodic System of the chemical elements as we continue to use nowadays (Fig. 2).

† Here and subsequently atomic weights of that time are indicated.

Nevertheless, there were clearly several unfilled positions in the Periodic System, and in the first publication on the Periodic Law Mendeleev already expressed the view that many then unknown elements existed, examples of which, for instance, should resemble aluminium and silicon, and have atomic weights of 65–75. Mendeleev was profoundly convinced that the best evidence that the main principles of the Periodic Law were correct was the fulfilment of predictions based on it. Two years after the discovery of this periodicity, therefore, he published a paper[3] in which he predicted in detail the physical and chemical properties of some hitherto undiscovered elements. "I have decided to do this so that, at least in time, when one of these bodies which I have predicted has been discovered, it will be possible finally to convince other chemists and myself of the rightness of the hypotheses underlying my proposed system". The most detailed examination was given to the expected properties of unknown analogues of boron, aluminium, and silicon, which were provisionally named by Mendeleev "ekaboron", "eka-aluminium", and "ekasilicon"‡.

The elements predicted by Mendeleev were very soon discovered. In 1875 the French chemist P. Lecoq de Boisbaudran discovered in a Pyrenean zinc blende a new element gallium, the properties of which coincided with those indicated by Mendeleev for eka-aluminium. In 1879 the Swedish chemist L. Nilson, while studying ytterbia earths, isolated from the Scandinavian minerals gadolinite and euxenite a new rare-earth element scandium, which proved to be ekaboron. In 1886 the German chemist C. Winkler, in analysing the mineral argyrodite, discovered in it a new element germanium, whose properties coincided extraordinarily closely with those predicted by Mendeleev for ekasilicon (Table 1). Winkler wrote: "It is hardly possible to find a more striking demonstration of the correctness of the concept of periodicity than the realisation of the hypothetical ekasilicon in the newly discovered element. This is not simply support for a daring theory: here we see an obvious extension of the chemical horizon, a powerful step in the field of knowledge".

Mendeleev described more briefly the expected properties of undiscovered analogues of manganese, tellurium, caesium, barium, lanthanum, and tantalum. Some of these elements—radium, actinium, and polonium—were discovered during his lifetime, and the others—technetium, rhenium, francium, and protactinium—only in the twentieth century.

At the end of the nineteenth century the Periodic System was subjected to a severe test, from which it emerged victorious. After Rayleigh and Ramsay had discovered argon in the air (1894), it appeared that this element could not find a place in the Periodic System. However, Ramsay's subsequent discovery of helium (in the gas expelled from the mineral cleveite) showed that a group of elements similar to argon existed.

In 1897 Ramsay gave a lecture on "A Still Undiscovered Gas". As he himself pointed out subsequently, in this lecture "following the example of our teacher Mendeleev, I described, as far as it was possible, the properties expected for and the presumable relations of the gaseous element which would fill the gap between helium and argon". Ramsay soon isolated this gas, of atomic weight 20, from liquid air, and called it *neon*. Heavy analogues of argon—krypton and xenon—were discovered almost simultaneously. According to the researches of that time all these elements were characterised by inertness—inability to enter into ordinary chemical reactions of oxidation and reduction—and the family of inert gases therefore found a place in the Periodic System as the newly formulated Group 0. In 1900 the radioactive element radon (radium emanation), discovered by A. Debierne, was added to this group.

‡ Here *eka* (Sanskrit) = "one" is used in the sense of the first adjacent analogue.

Table 1. Properties of germanium predicted and found.

Property	Predicted for ekasilicon	Found for germanium
Atomic weight	Es = 72	Ge = 72.60
Valency	quadrivalent, but can exhibit also a lower valency	4 and 2
Free element		
Atomic volume	about 13	13.5
Specific gravity	about 5.5	5.36
Fusibility and volatility	"fusible metal, able to volatilise at a high temperature"	b.p.958.5°C m.p.2700°C
Highest oxide	EsO_2	GeO_2
Molecular volume	about 22	22.2
Specific gravity	4.7	4.703
Chemical properties	acidic and extremely weakly basic	amphoteric with acidic properties predominating
Highest chloride	$EsCl_4$	$GeCl_4$
Boiling point	close to 90°C	83.1°C
Specific gravity	about 1.9	1.874
Chemical properties	decomposed by water	readily hydrolysed by water
Hydrogen compounds	"a hydrogen compound can also be greatly expected" "EsH_4 should decompose readily into hydrogen and the metal"	GeH_4 and other germanium hydrides obtained GeH_4 decomposes at 350°C
Organometallic compounds	"it will, of course, form organometallic compounds"	many organometallic compounds of germanium
$(C_2H_5)_4R$, b.p.	160°C	163.5°C
$(C_2H_5)_4R$, sp. gr.	0.96	0.99

The discovery of elements predicted by Mendeleev, the exact coincidence of their properties with those calculated on the basis of the Periodic Law, and the confirmation of the corrections made by Mendeleev to atomic weights—all this reinforced the materialist view of the chemical elements, and immeasurably extended the possibilities of the understanding of Nature by man. The Periodic System became a powerful weapon for use by research workers in the further development of chemistry and physics.

Various properties of the chemical elements and their compounds began to be correlated on the basis of the Periodic Law. In 1869 Mendeleev demonstrated periodicity in the structure of compounds formed by elements, i.e. in the most important chemical property, the valency. He even established periodicity in the specific gravities and atomic volumes of elements. Other workers showed that the melting points of elements vary periodically, and this was noted also for the melting points of metal chlorides. The quantity of heat involved on formation of chlorine, bromine, and iodine compounds was found to vary periodically with increasing atomic weight of the elements interacting with the halogens.

In 1889 Mendeleev directed attention also to the periodicity of structure of the spectra of elements as a function of their atomic weights. A relation was observed between the position of elements in the Periodic System and their

Періодическая система элементовъ по группамъ и рядамъ.

Ряды.	ГРУППЫ ЭЛЕМЕНТОВЪ:								
	0	I	II	III	IV	V	VI	VII	VIII
1	—	Водо-родъ. H 1.008	—	—	—	—	—	—	
2	Гелій. He 4.0	Литій. Li 7.03	Берилій. Be 9.1	Боръ. B 11.0	Углеродъ. C 12.0	Азотъ. N 14.01	Кислородъ. O 16.00	Фторъ. F 19.0	
3	Неонъ. Ne 19.9	Натрій. Na 23.05	Магній. Mg 24.36	Алюминій. Al 27.1	Кремній. Si 28.2	Фосфоръ. P 31.0	Сѣра. S 32.06	Хлоръ Cl 35.45	
4	Аргонъ. Ar 38	Калій. K 39.15	Кальцій. Ca 40.1	Скандій. Sc 44.1	Титанъ. Ti 48.1	Ванадій. V 51.2	Хромъ. Cr 52.1	Марганецъ. Mn 55.0	Желѣзо. Fe 55.9 / Кобальтъ. Co 59 / Никкель. Ni 59 (Cu)
5		Мѣдь Cu 63.6	Цинкъ. Zn 65.4	Галлій. Ga 70.0	Германій. Ge 72.5	Мышьякъ. As 75	Селенъ. Se 79,2	Бромъ. Br 79.95	
6	Криптонъ. Kr 81.8	Рубидій. Rb 85.5	Стронцій. Sr 87.6	Итрій. Y 89.0	Цирконій. Zr 90.6	Ніобій. Nb 94.0	Молибденъ. Mo 96.0	—	Рутеній. Ru 101.7 / Родій Rh 103.0 / Палладій. Pd 106,5 (Ag)
7		Серебро. Ag 107.93	Кадмій. Cd 112.4	Индій. In 115.0	Олово. Sn 119.0	Сурьма. Sb 120.2	Теллуръ. Te 127	Іодъ. J 127	
8	Ксенонъ. Xe 128	Цезій. Cs 132.9	Барій. Ba 137.4	Лантанъ. La 138.9	Церій. Ce 140.2	—	—	—	— — —
9		—	—	—	—	—	—	—	
10	—	—	—	Иттербій. Yb 173	—	Тантанъ. Ta 183	Вольфрамъ. W 184	—	Осмій. Os 191 / Иридій. Jr 193 / Платина. Pt 194.8 (Au)
11		Золото. Au 197.2	Ртуть. Hg 200.0	Талій. Tl 204,1	Свинецъ, Pb 206.9	Висмутъ. Bi 208.5	—	—	
12	—	—	Радій. Rd 225	—	Торій. Th 232.5	—	Уранъ. U 238.5		
	Высшіе солеобразные окислы: [*]								
	R	R^2O	RO	R^2O^3	RO^2	R^2O^5	RO^3	R^2O^7	RO^4
	Высшія газообразныя водородныя соединенія: [**]								
					RH^4	RH^3	RH^2	RH	

Figure 3. Mendeleev's Periodic System of the elements (1905).

* Highest saltlike oxides.

** Highest gaseous hydrogen compounds.

magnetic properties. Investigations of copper alloys by A. A. Baikov (1902) showed the applicability of periodicity principles to the composition of the intermetallic compounds formed in alloys.

For many years after the discovery of the Periodic Law Mendeleev continued to improve the appearance of his table, using both short and long forms. Fig. 3 shows the last table drawn up by Mendeleev not long before his death in 1907.

Even during Mendeleev's lifetime the Periodic Law and the system of elements based on it achieved immense success. However, several sites in the system still remained obscure. It was unknown whether elements should exist between hydrogen and helium, and the number of rare-earth elements, as also their position in the Periodic System, was indefinite. In view of all these difficulties it was impossible to compute the total number of elements between hydrogen and uranium. The actual

cause of the periodicity was obscure. One must be amazed by the genius of Mendeleev, who was able to set up the Periodic System of the elements in the almost complete absence of information on the structure of matter, and to set it up in such a way that even after a century it has not required any fundamental changes.

Since Mendeleev's death the Periodic Law has exerted an immense influence on the development of the work of physicists and chemists on the structure of matter.

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We must first note the part played by the Periodic System in unravelling the phenomenon of radioactivity and elucidating the nature of isotopes. The discovery by Becquerel in 1896 of "uranium rays" with their remarkable properties led to many investigations in this new branch of science. Another heavy element, thorium, also proved to be radioactive. In 1898 Marie and Pierre Curie discovered in uranium ores two new elements—radium and polonium—exhibiting still stronger radioactivity than uranium. They isolated a pure preparation of radium from residues from the processing of uranium ore. This element proved to be an analogue of barium, and corresponded in properties to Mendeleev's ekabarium. The properties of polonium were very close to those of ekatellurium.

In 1899 Debierne discovered yet another radioactive element, actinium, an analogue of lanthanum. The existence of this element had been predicted by Mendeleev as early as 1871.

It was established in 1900 that radium preparations evolve continuously a radioactive gas—radium emanation—which proved to be analogous to xenon in Group 0 of the Periodic System, and is now called *radon*. A remarkable property of radon is its rapid disintegration, which is half complete in 3.85 days. Ramsay and Soddy discovered in 1902 that, after radium emanation has been sealed in a discharge tube for some time, it begins to show the spectrum of helium. This was the first experimentally proved case of the transmutation of elements.

Mendeleev referred very doubtfully to the possibility of the interconversion of elements, pointing out that all reports of this kind require especially careful checking and usually are not confirmed. Nevertheless, he regarded himself as "not an opponent, but rather inclined to accept the concept of the complexity of elements". He wrote (1898) that "it would be extremely interesting to be present when data are established to prove the interconversion of elements, because I could then hope that the cause of the periodic regularity would be discovered and understood". As we shall see, the development of science made this task urgent within a few years.

In 1902, on the basis of a detailed study of the radioactivity of thorium, Rutherford and Soddy put forward the hypothesis that radioactive phenomena are due to transformations of atoms and hence of elements. Subsequent investigations completely confirmed this suggestion.

The study of radium emanation showed that the so called "active residue" remaining after its disintegration contained several elements differing from one another in radioactive properties, i.e. in the character and energy of the emission. Many radioactive elements were detected in studying the changes undergone by uranium, actinium, and thorium.

Only a proportion of the newly discovered radioactive elements could be placed in empty positions in the Periodic System. Examination of a large number of the radioactive elements which were members of the various radioactive series established that many of them, while differing in radioactive properties, could not be separated from one another or from certain ordinary elements by chemical methods. For example, one of the products of the disintegration of uranium—the radioactive element ionium—while differing in its radioactivity from thorium could not be distinguished from it chemically. One of the initial products in the disintegration of thorium—the so called radiothorium—disintegrated immeasurably more rapidly than thorium, but chemically was completely identical with it. It thus appeared that many newly discovered radioactive elements did not differ in chemical properties from uranium, thorium, radium, lead, bismuth, and other elements in the last two rows of the Periodic System. Hence one chemical element corresponded to more than one type of atoms, differing in mass and in rate of radioactive disintegration.

In 1913 Soddy suggested the name *isotopes* ("isos" = same, "topos" = place) for such varieties of elements, to indicate that they occupy the same place in the Periodic System.

The numerous radioactive elements formed in the disintegration of uranium, thorium, or actinium were now combined into series strictly related to Mendeleev's Periodic System. Each α-emission gave a product which was an isotope of an element located two places nearer to the beginning of the Periodic System. As a result of β-disintegration an element was obtained one place closer to the end of the system. This so called Fajans displacement law enabled many new radioactive elements to be discovered, and introduced order into obscure positions in radioactive series.

Electromagnetic analysis of a beam of canal rays by Thomson in 1913 yielded, with neon as example, the first information on the existence of isotopes of non-radioactive elements. Aston's development of the design of the mass spectrograph enabled isotopes of several ordinary elements to be detected.

The phenomenon of isotopy gave a additional content to the Periodic System. The ideas of A. M. Butlerov, W. Crookes, and other scientists on the possibility of varieties of atoms of the same element, differing in mass, were brilliantly confirmed. Furthermore, the subsequent observation of an appreciable difference in chemical properties between the isotopes of hydrogen opened a new chapter in science—the chemistry of isotopes, closely connected with the Periodic System.

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The discovery of the phenomena of radioactivity and the vigorous development of atomic physics at the beginning of the twentieth century led, as is known, to the nuclear theory of atomic structure (Rutherford 1911), the discovery of the law relating the wavelengths of the characteristic X-ray spectra of elements to the charges on their atomic nuclei (Moseley 1913), and the working out of the principles underlying the quantum theory of atomic structure (Bohr 1913). The Periodic Law had an extraordinary influence on the development of these scientific trends, since it gave investigators a natural system of chemical elements with all the structural regularities of atoms latent in it.

On the other hand, the contemporaneous theory of atomic structure explained the reasons for the phenomenon of periodicity itself, and improved still further the methods for predicting the properties of unknown elements. The

experimental determination of the charges on atomic nuclei, based on Moseley's law, was especially important. It provided an exact method for determining the atomic numbers of the elements in the Periodic System and establishing the total number of elements between hydrogen and uranium. The correctness of the arrangement of all the elements in Mendeleev's table was confirmed. The atomic number of iodine (53) proved to be higher than that of tellurium (52). In 1914 empty spaces remained in the Periodic System at Nos. 43, 61, 72, 75, 85, 87, and 91, of which Nos. 61, 72, 75, and 85 belonged to the third long period.

The theory of atomic structure explained the peculiar position in the Periodic System of the rare-earth metals which follow lanthanum in the third long period. It turned out that, in this part of the system, successive electrons in the atoms of elements beginning with cerium enter a lower electron shell of the fourth energy level at the 4*f*-sublevel, which may contain up to fourteen electrons and is completed at lutetium. The number of valency electrons remains unchanged, being three as in lanthanum. At the present time, therefore, it is usual to group the elements in the cerium–lutetium family under the name *lanthanides*. They fit into the same space as lanthanum, and are listed as a separate series below the table.

Table 2. Structure of electron shells in atoms of rare-earth metals.

Element	Atomic No.	Energy levels in atoms											
		n=1	*n*=2	*n*=3		*n*=4				*n*=5			*n*=6
		K	*L*	*M*		*N*				*O*			*P*
		s	*s*, *p*	*s*, *p*	*d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*s*
Sc	21	2	8	8	1	2							
Y	39	2	8	8	10	2	6	1		2			
La	57	2	8	8	10	2	6	10		2	6	1	2
Ce	58	2	8	8	10	2	6	10	2	2	6		2
Pr	59	2	8	8	10	2	6	10	3	2	6		2
Nd	60	2	8	8	10	2	6	10	4	2	6		2
Pm	61	2	8	8	10	2	6	10	5	2	6		2
Sm	62	2	8	8	10	2	6	10	6	2	6		2
Eu	63	2	8	8	10	2	6	10	7	2	6		2
Gd	64	2	8	8	10	2	6	10	7	2	6	1	2
Tb	65	2	8	8	10	2	6	10	9	2	6		2
Dy	66	2	8	8	10	2	6	10	10	2	6		2
Ho	67	2	8	8	10	2	6	10	11	2	6		2
Er	68	2	8	8	10	2	6	10	12	2	6		2
Tm	69	2	8	8	10	2	6	10	13	2	6		2
Yb	70	2	8	8	10	2	6	10	14	2	6		2
Lu	71	2	8	8	10	2	6	10	14	2	6	1	2

Note. *n* is the principal quantum number; *K*, *L*, *M* are energy levels in the atoms; *s*, *p*, *d*, *f* are groups of electrons.

The structure of the electron shells in atoms of the rare-earth metals, based on present-day results, is set out in Table 2. It is seen that two valency electrons of the lanthanides belong to the 6*s*-sublevel, while the third is usually detached from the 4*f*-sublevel and is located in the 5*d*-sublevel only for a few members of this series. At the start of formation of the 4*f*-shell the electrons in it are not very firmly bound. As a consequence cerium, praseodymium, and probably neodymium are capable of forming compounds in which they are quadrivalent. After this the increasing charge on the nucleus strengthens the structure of this shell. It must be added that the shell is apparently completed in two layers, each comprising seven electrons. Ability to form compounds of higher valency is therefore exhibited also by terbium, which is characterised by completion of the second layer. The elements preceding gadolinium (samarium, europium) and lutetium (ytterbium), on the other hand, may approach a more stable configuration by splitting off a smaller number of electrons, and are therefore bivalent under certain conditions.

Subsequent investigations established an important rule for the variation in size of the lanthanide atoms [4]. Electrons entering the inner 4*f*-layer do not completely screen the increasing nuclear charge. The electrons in the outer shells are therefore drawn towards the nucleus, and the overall size of the atom diminishes (lanthanide contraction). The ionic radii for the rare-earth metals in the tervalent state are given below.

Ionic radius, Å

Sc	Y	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
0.68	0.88	1.04	1.02	1.00	0.99	(0.98)	0.97	0.96	0.94	0.92	0.91	0.89	0.87	0.86	0.85	0.8

The phenomenon of the lanthanide contraction results in a weakening of the basic properties of the hydroxides in the sequence lanthanum–lutetium. Whereas lanthanum hydroxide is similar in properties to strontium hydroxide, lutetium hydroxide is a weak base, approaching in this respect the hydroxide of scandium, which is located far higher in the same group of the Periodic System. Dysprosium and holmium are similar to yttrium in this respect.

Thus the similarity in structure of the outer electron shell of the atoms and the lanthanide contraction converted scandium, yttrium, lanthanum, and the lanthanides into a closely intertwined tangle of elements, greatly resembling one another in properties and in natural occurrence. This in turn was responsible for all the difficulties involved in their separation, purification, and identification.

The theory of atomic structure made it clear that element No. 72, immediately following lutetium, should have two valency electrons in each of the sublevels 6*s* and 5*d*, and would therefore be quadrivalent, an analogue of zirconium, not a rare-earth metal. A search in zirconium preparations undertaken by G. Hevesy and D. Coster on this basis using X-rays proved successful, and in 1923 the element was discovered and named *hafnium* (Hf = 178.5). It is noteworthy that an analogue of zirconium of atomic weight 180 had been envisaged by Mendeleev in the very first form of his table (see above).

Thus the bundle of rare-earth elements in the Periodic System was disentangled. Elements which were missing from the Periodic Table at the time when Moseley's law was discovered were either isolated from natural minerals or synthesised by nuclear reactions within a fairly short period.

In 1918 L. Meitner and O. Hahn isolated the radioactive element No. 91, protactinium, from the processing wastes of a uranium ore. In 1925 W. Noddack, I. Tacke, and O. Berg detected element No. 75 in specimens of native platinum, tantalite, and molybdenite, and termed it *rhenium*. The discovery by these workers of element No. 43 was not subsequently confirmed. This latter element was found in 1937 by C. Perrier and E. Segrè in a sample of molybdenum which had undergone prolonged irradiation with a powerful beam of deuterons in a cyclotron. The nuclear reaction was represented by the scheme ${}_{42}\mathrm{Mo}(d, n)43$. After identification the element was named *technetium* to emphasise its artificial production. Considerable quantities of technetium were subsequently found in fission fragments from uranium, and it can be extracted from waste products of the atomic industry.

In 1939 Mlle Perey was studying the natural radioactive disintegration products from actinium, and found in them a radioactive isotope (half-life 21 min), similar in chemical behaviour to caesium. This proved to be element

No. 87—the ekacaesium predicted by Mendeleev—and was termed *francium*.

A radioactive isotope of ekaiodine—element No. 85 (half-life 7.5 h)—was discovered in 1940 by D. R. Corson, K. R. MacKenzie, and E. Segrè by bombarding bismuth with accelerated helium nuclei of energy 38 MeV. The process was represented by $^{209}_{83}Bi(^{4}_{2}He, 2n)^{211}85$. The name *astatine*, given to this element, is an indication of its instability.

Finally element No. 61, which had been unsuccessfully sought for a long time by many chemists in rare-earth preparations, was discovered in 1947 among the fission products of uranium. It was identified by J. A. Marinsky, L. E. Glendenin, and C. D. Coryell in the form of two radioactive isotopes having half-lives of 55 h and 2.6 years. The element acquired the name *promethium* in commemoration of the practical utilisation of atomic energy, which the authors compared with theft of fire by Prometheus.

Thus by 1947 all the places between hydrogen and uranium in the Periodic System had been filled.

Completely new problems facing the Periodic System arose in connection with the successful development of the synthesis of new heavy elements[5]. It is noteworthy that Mendeleev admitted the possibility of extending the Periodic System beyond uranium, and this suggestion of his has been justified.

The idea of synthesising transuranic elements became topical in the 1930s, when E. Fermi and his coworkers developed a method for the artifical production of radioactive isotopes by means of slow neutrons. In 1935 they detected in neutron-irradiated uranium several short-lived β-radioactive isotopes, one of which (half-life 13 min) was coprecipitated with manganese and rhenium, and was assumed to be an analogue of rhenium $^{239}_{93}$EkaRe. However, further investigations by L. Meitner, O. Hahn, and F. Strassmann showed that in these experiments many radioactive isotopes—fission products of uranium—are formed, which are coprecipitated with various elements. Among them a β-emitter was found (half-life 23 min), identical in chemical properties with uranium and assumed to be an isotope $^{239}_{92}U$. As a result of β-disintegration it should have been converted into element No. 93. However, these workers were unable to detect a new element here, owing to the weakness of the neutron source used.

Element No. 93, given the name *neptunium* (Np), was discovered by E. D. McMillan and P. H. Abelson in 1940 by irradiating thin layers of ammonium uranate with a powerful beam of neutrons obtained by bombarding a beryllium target with deuterons of energy 16 MeV in the large cyclotron at the University of California. Fragments arising from the fission of uranium were removed by the recoil phenomenon. Two types of β-activity, having half-lives of 23 min and 2.9 days, were detected in the uranium preparation. The nature of the first was known, being due to $^{239}_{92}U$. Conversion of the first into the second emitter served as proof of the formation of element No. 93. McMillan and Abelson concluded that neptunium was not an analogue of rhenium. It was found to have at least two states of oxidation, in the lower of which neptunium resembled the rare-earth metals, whereas in the higher state of oxidation it was similar to uranium.

The β-disintegration of neptunium must be expected to yield element No. 94, which was named *plutonium* (Pu). The first isotope of the latter $^{238}_{94}Pu$ (half-life 89.6 years) was synthesised at the end of 1940 by G. T. Seaborg, E. D. McMillan, J. W. Kennedy, and A. C. Wahl by bombarding uranium with deuterons in a cyclotron. The neptunium isotope $^{238}_{93}Np$ (half-life 2.1 days) was obtained as an intermediate product:

$$_{92}U^{238} + {}_{1}H^{2} = {}_{93}Np^{238} + 2n; \quad {}_{93}Np^{238} = {}_{94}Pu^{238} + \bar{\beta} \ .$$

The most important chemical properties of the new element and the principles of its separation from uranium were studied on tracer quantities of the above isotope. In its highest valency plutonium resembles uranium, but is more readily reduced. The properties of the compounds of lower valency recall thorium and the rare-earth metals. For military reasons the first information on plutonium was published only in 1946.

In 1941 a longer-lived isotope of plutonium ^{239}Pu (half-life 24 360 years), capable of fission by slow neutrons, was discovered after the prolonged bombardment of uranium with deuterons in a cyclotron. As a consequence of the above properties it subsequently acquired practical value as a form of atomic fuel.

Painstaking work on the irradiation of a few tens of kilogrammes of uranyl nitrate with neutrons in a cyclotron resulted by the end of 1942 in the isolation of 0.5 mg of plutonium in the form of pure compounds. These investigations were continued in the first laboratory uranium reactor, which became operative on 2nd December 1942 in the University of Chicago. At the same time planning went ahead for a pilot plant to isolate plutonium from uranium irradiated in the reactor, with an enrichment factor of 10^{10}, which was unprecedented in the chemical industry. The first factory-scale reactor was started up after a year. Less than seven weeks later an experimental separation plant began to operate, and plutonium was soon available to the research workers in gramme quantities. In September 1944 the first works began to operate to produce kilogrammes of plutonium. Thus less than three years elapsed between the first artificial separation of the new element and the organisation of its isolation on an industrial scale! Nowadays plutonium is manufactured in several countries, and its production is measured in many tons per annum.

The development of further investigations on the transuranium elements is due to the work of the distinguished American scientist Seaborg and his collaborators. During 1944–1955 seven further transuranium elements were discovered. Americium (Am, No. 95) was obtained by irradiating plutonium with neutrons; and curium (Cm, No. 96), berkelium (Bk, No. 97), and californium (Cf, No. 98) by the bombardment with high-energy helium ions of targets containing plutonium, americium, and curium respectively. Isotopes of einsteinium (Es, No. 99) and fermium (Fm, No. 100) were first detected when uranium was irradiated with a very intense instantaneous flux of neutrons during the thermonuclear explosion produced in 1952. Many repeated neutron captures resulted in the formation of very heavy isotopes of uranium, which then disintegrated with the emission of β-particles and the formation of several transuranium elements, including einsteinium and fermium. These elements were later synthesised by other routes. Element No. 101 was obtained by the action of high-energy (41 MeV) helium ions on einsteinium. In the first experiments seventeen atoms in all of the new element were identified from its conversion into fermium. The discoverers gave the name *mendelevium* (Md) to element No. 101 "in honour of the leading part played by the great Russian chemist Dmitrii Mendeleev, who was the first to use the Periodic System of the elements to predict the chemical properties of hitherto undiscovered elements—a principle which gives the key to the discovery of the last seven transuranic elements (actinides)...".

Table 3 indicates the nuclear reactions first used to obtain the transuranium elements, together with their discoverers.

The first information on the discovery of element No. 102 appeared in 1957. A group of research workers—P.R. Fields, J. Milsted, H. Atterling, et al.—irradiated a preparation from curium with carbon-13 ions:

$$_{96}Cm^{244}(C^{13}, 6n)\,102^{251} \quad \text{or} \quad _{96}Cm^{244}(C^{13}, 4n)\,102^{253}.$$

The products of the nuclear reaction had a half-life of about 10 min. The name *nobelium* (No) was proposed for the new element. However, these results were not confirmed when checked in Seaborg's laboratory.

Table 3. History of the discovery of the transuranium elements.

Element	Atomic No.	Year	Nuclear reactions	Discoverers
Np	93	1940	$_{92}U^{238}(n, \gamma)_{92}U^{239}$; $_{92}U^{239} = {}_{93}Np^{239} + \bar{\beta}$	E.D.McMillan and P.H.Abelson
Pu	94	1940	$_{92}U^{238}(H^2, 2n)_{93}Np^{238}$; $_{93}Np^{238} = {}_{94}Pu^{238} + \bar{\beta}$	G.T.Seaborg, E.D.McMillan, J.W.Kennedy, and A.C.Wahl
Am	95	1944	$_{94}Pu^{239} + 2n = {}_{94}Pu^{241}$; $_{94}Pu^{241} = {}_{95}Am^{241} + \bar{\beta}$	G.T.Seaborg, R.H.James, L.O.Morgan, and A.Ghiorso
Cm	96	1944	$_{94}Pu^{239}(_2He^4, n)_{96}Cm^{242}$	G.T.Seaborg, R.H.James, and A.Ghiorso
Bk	97	1949	$_{95}Am^{241}(_2He^4, 2n)_{97}Bk^{243}$	S.G.Thompson, A.Ghiorso, and G.T.Seaborg
Cf	98	1950	$_{96}Cm^{242}(_2He^4, n)_{98}Cf^{245}$	S.G.Thompson, K.Street, A.Ghiorseo, and G.T.Seaborg
Es	99	1955	$_{92}U^{238} + 15n = {}_{92}U^{253}$; $_{92}U^{253} \xrightarrow[6\bar{\beta}]{} {}_{98}Cf^{253} \rightarrow {}_{99}Es^{253}$	A.Ghiorso, S.G.Thompson, G.H.Higgins, and G.T.Seaborg
Fm	100	1955	$_{92}U^{238} + 17n = {}_{92}U^{255}$; $_{92}U^{255} \xrightarrow[7\bar{\beta}]{} {}_{99}Es^{255} \xrightarrow{\bar{\beta}} {}_{100}Fm^{255}$	ditto
Md	101	1955	$_{99}Es^{253}(_2He^4, _1)_{101}Md^{256}$	A.Ghiorso, B.Harvey, G.Choppin, S.G.Thompson, and G.T.Seaborg
No?	102	1957	$_{96}Cm^{244}(C^{13}, 4n)\,102^{253}$; $_{96}Cm^{246}(C^{13}, 4n)\,102^{254}$; $_{94}Pu^{241}(_6O^{16}, 4n)\,102^{253}$	various workers
Lr	103	1961	$_{98}Cf^{252}(B^{11}, 6n)\,103^{257}$; $_{98}Cf^{250}(B^{10}, 3n)\,103^{257}$	A.Ghiorso, T.Sikkeland, A.Larsh, and R.Latimer
Ku	104	1966	$_{94}Pu^{242}(_{10}Ne^{22}, 4n)\,104^{260}$	G.N.Flerov, N.A.Dugin, I.Zvara, *et al.*

In the same year G. N. Flerov, S. M. Polikanov, A. S. Karamyan, et al. in the USSR irradiated plutonium-241 with a flux of quintuply charged oxygen ions and detected α-particles of energy 8–9 MeV, which could be attributed to an isotope $^{253}102$ having a half-life between a few seconds and 1 min. No chemical identification was made.

During 1958–1959 Ghiorso, Seaborg, et al. made repeated attempts to obtain isotopes of element No. 102 by the reactions

$$_{96}Cm^{246}(C^{12}, 4n)\,102^{254} \quad \text{or} \quad _{96}Cm^{244}(C^{13}, 4n)\,102^{253}$$

but detected only products having half-lives of a few seconds. The authors of the original communication on element No. 102 also changed their view, and came to think that the isotope $^{255}102$ had been obtained in their experiments. In 1963 the Soviet scientists G. N. Flerov, E. D. Donets, V. A. Shchegolev, et al. synthesised an isotope of element No. 102 having mass number 256 in a powerful accelerator of multicharged ions. Metallic uranium was bombarded with high-energy neon nuclei. The half-life of the new isotope proved to be close to 8 min. Thus the question of the synthesis of element No. 102 had been considerably clarified, but its name is still under discussion.

At the beginning of 1961 a paper appeared by A. Ghiorso, T. Sikkeland, A. Larsh, and R. Latimer on the discovery of element No. 103, named *lawrencium* (Lr). These workers bombarded a target containing 3 mg of a mixture of californium isotopes with boron (^{10}B and ^{11}B) nuclei of energy 10.3 MeV in the large cyclotron at Berkeley. An α-emitter was formed with a half-life of 8 ± 2 s, the energy of the α-particles being 8.6 MeV. Calculations led to the conclusion that an isotope of element No. 103 having mass number 257 was formed. A longer-lived isotope $^{256}_{103}Lr$ (half-life 35 s) was also obtained later.

In 1966 G. N. Flerov, N. A. Dugin, I. Zvara, et al., working at the Joint Institute for Nuclear Research (at Dubna), synthesised the first atoms of element No. 104. A plutonium-242 preparation was irradiated with neon-22 ions of energy 115 MeV on a cyclotron. The nuclear reaction $^{242}Pu(^{22}_{10}Ne, 4n)^{260}104$ took place. The isotope obtained underwent spontaneous fission with a half-life of 0.3 s. It was detected from the tracks made by the fission fragments in glass or mica. It was identified chemically from the volatility of the chlorine compounds (see below). Element No. 104 received the name *kurchatovium* (Ku).

Table 4. Initially discovered and longest-lived isotopes of transuranium elements.

Atomic No. Z	Element	Initially discovered isotope		Longest-lived isotope	
		A	$T_{1/2}$	A	$T_{1/2}$
93	Np	239	2.3 days	237	$2.2 \cdot 10^6$ years
94	Pu	238	86.4 years	244	$7.6 \cdot 10^7$ years
95	Am	241	458 years	243	$8 \cdot 10^3$ years
96	Cm	242	162.5 days	247	$1.6 \cdot 10^7$ years
97	Bk	243	4.5 h	247	$1.4 \cdot 10^3$ years
98	Cf	244	2.5 min	251	800 years
99	Es	246	7.3 min	254	480 days
100	Fm	254	3.2 h	257	95 days
101	Md	256	30 min	258	54 days
102	No?	256	8 min	—	—
103	Lr	257	8 s	256	35 s
104	Ku	260	0.3 s	—	—

Thus twelve transuranic elements, having atomic numbers 93–104, are now known. It is significant that their first isotopes to be isolated were usually short-lived, after which methods were found for obtaining longer-lived isotopes (Table 4). It may be supposed that this rule will apply also to the most remote transuranic elements.

The principal method for obtaining large quantities of transuranic elements is the irradiation of ordinary uranium, uranium enriched with its isotope of mass 235, or plutonium with a high-power flux of neutrons in a nuclear reactor. The method of subterranean explosions, in which extraordinarily powerful fluxes of neutrons are produced, is of value for certain far transuranic elements, e.g. fermium-257 (half-life 95 days). In this case, however, the resulting isotope must be extracted from a large quantity of rocks which have fused together during the explosion.

Nowadays the annual production of plutonium throughout the world amounts to many tons. Neptunium, a by product of the manufacture of plutonium, is obtained in tens of kilogrammes. Americium is available in kilogramme

quantities, and curium in tens and hundreds of grammes; milligrammes of berkelium and californium have been isolated, and microgrammes of einsteinium and fermium. Mendelevium (atomic number 101), element No. 102, and lawrencium (atomic number 103) are studied in tracer amounts. The question can already be posed now of expanding scientific research and developing practical applications for many transuranic elements.

The position of the transuranic elements in the Periodic System is closely connected with the structure of their atoms and the valency they exhibit. The theory of atomic structure envisages that the inner 5*f*-layer, analogous to the 4*f*-layer formed in the lanthanides, should be filled with electrons at the beginning of the fourth long period in Mendeleev's system.

Table 5. Structure of electron shells in actinide atoms.

Element	Atomic No. Z	Energy levels and groups of electrons in atoms									
		n=1	n=2	n=3	n=4	n=5		n=6			n=7
		K	L	M	N	O		P			Q
		s	s, p	s, p, d	s, p, d, f	s, p, d	f	s	p	d	s
Ac	89	2	8	18	32	18	—	2	6	1	2
Th	90	2	8	18	32	18	—	2	6	2	2
Pa	91	2	8	18	32	18	2	2	6	1	2
U	92	2	8	18	32	18	3	2	6	1	2
Np	93	2	8	18	32	18	4	2	6	1	2
Pu	94	2	8	18	32	18	6	2	6	—	2
Am	95	2	8	18	32	18	7	2	6	—	2
Cm	96	2	8	18	32	18	7	2	6	1	2
Bk	97	2	8	18	32	18	9	2	6	—	2
Cf	98	2	8	18	32	18	10	2	6	—	2
Es	99	2	8	18	32	18	11	2	6	—	2
Fm	100	2	8	18	32	18	12	2	6	—	2
Md	101	2	8	18	32	18	13	2	6	—	2
No?	102	2	8	18	32	18	14	2	6	—	2
Lr	103	2	8	18	32	18	14	2	6	1	2

In 1945 Seaborg suggested that this filling begins after actinium, resulting in a group of elements, having atomic numbers 90–103, similar to the lanthanides, which have been termed *actinides*. The actinide theory envisages an analogy between corresponding elements in the lanthanide and actinide families. However, the valency properties of the actinides have proved to be more complicated. With thorium, protactinium, and uranium the most characteristic compounds correspond to the higher valency indicated by the numbers of the groups in which Mendeleev placed them (Groups IV–VI respectively). Spectral investigations by W. F. Meggers (1947) showed that the first 5*f*-electrons probably appear only when protactinium is reached. W. H. Zachariasen's crystallographic measurements (1954) even led to the conclusion that metallic thorium, protactinium, and uraniun contain no 5*f*-electrons, and that metallic neptunium contains only one 5*f*-electron. On the other hand, the magnetic properties indicate the presence of 5*f*-electrons beginning with uranium. It is probable that the strength of bonding of 5*f*- and 6*d*-electrons is closely similar in the atoms of actinides. Furthermore, it is obviously weaker than that of 4*f*-electrons in the lanthanides.

Table 5 contains up-to-date information on the atomic structure of the actinides. For many of the elements, however, especially the higher actinides, these values are hypothetical, and have not yet been confirmed experimentally.

The original investigation of neptunium and plutonium had established that these elements exhibit variable valency—from 6 to 3—neptunium being mainly quinquevalent, and plutonium quadrivalent. It was supposed that all subsequent actinides would be tervalent. However, compounds of americium were soon obtained in which this element exhibited valencies of 4, 5, and 6, as well as compounds of quadrivalent curium and berkelium. The valencies of lanthanides and actinides are compared in Table 6.

Table 6. Valency of lanthanides and actinides.

Lanthanides			Actinides		
symbol	atomic no.	valency	valency	atomic no.	symbol
Ce	58	**3**, 4	**3**, 4	90	Th
Pr	59	**3**, 4	3, 4, **5**	91	Pa
Nd	60	**3**	3, 4, 5, **6**	92	U
Pm	61	**3**	3, 4, **5**, 6, 7	93	Np
Sm	62	2, **3**	3, **4**, 5, 6, 7	94	Pu
Eu	63	2, **3**	(2), **3**, 4, 5, 6	95	Am
Gd	64	**3**	**3**, 4	96	Cm
Tb	65	**3**, 4	**3**, 4	97	Bk
Dy	66	**3**	3, (4)	98	Cf
Ho	67	**3**	**3**	99	Es
Er	68	**3**	**3**	100	Fm
Tm	69	**3**	2, **3**	101	Md
Yb	70	2, **3**	2, **3**	102	No
Lu	71	**3**	**3**	103	Lr

N. N. Krot and A. D. Gel'man have recently (1967) made the important discovery that neptunium and plutonium can exist in the septivalent state. If aqueous suspensions of neptunates(VI) and plutonates(VI)—K_2NpO_4 and K_2PuO_4—are oxidised with ozone in strongly alkaline medium, the deposits gradually dissolve to form dark green solutions of neptunates(VII) and plutonates(VII): e.g.

$$2K_2NpO_4 + O_3 + 2KOH = 2K_3NpO_5 + O_2 + H_2O \quad .$$

Several compounds of septivalent neptunium and plutonium have been obtained in the solid state from these solutions—$[Co(NH_3)_6]NpO_5.3H_2O$, $[PtCl(NH_3)_5]NpO_5$, $Sr_3(NpO_5)_2.nH_2O$, $Ba_3(NpO_5)_2.nH_2O$, $Ba_3(PuO_5)_2.nH_2O$—neptunium(VII) compounds being dark green, and plutonium(VII) compounds brownish black. They exhibit strong oxidising properties, this applying especially to septivalent plutonium. The oxidation of neptunium and plutonium to the septivalent state can be effected not only with ozone but also with hypochlorite, hypobromite, xenon compounds, and other active oxidants, necessarily in strongly alkaline medium.

A carrier method has recently been used to study the valency states of the shortest-lived far actinides, which have been used either in tracer quantities or as solitary atoms[6]. A bivalent state was found from entrapment with a barium sulphate precipitate, and tervalent and quadrivalent states were shown by extraction with 4-methylpentan-2-one or other solvent. The experiments showed that in aqueous solution mendelevium ($Z = 101$) occurs in the tervalent form, but can easily be reduced to the bivalent state with zinc dust, bivalent chromium, and other reductants. This distinguishes mendelevium from its formal lanthanide analogue thulium, with which the bivalent state is unknown.

In nitrate solutions element No. 102 was found to exist solely in the bivalent form, strong oxidising agents being required to convert it into the tervalent state. Here, too,

a fundamental difference from the properties of the lanthanide analogue, ytterbium, is observed.

Preliminary experiments on a small number of lawrencium atoms ($Z = 103$) indicated that this element is probably stably tervalent, although the possibility of its reduction or oxidation is not excluded. Lawrencium completes the family of actinides, and it should be similar to lutetium, which is characterised by tervalency.

The difference in properties, notably in valency, between lanthanides and actinides cannot be regarded as unexpected. It is completely explicable in terms of Mendeleev's Periodic Law. In each group of the Periodic System increase in the atomic numbers of analogous elements is accompanied by a definite change in their physical and chemical properties. This applies not only to individual elements but also to groups thereof, an example being the ionisation potentials (Fig. 4).

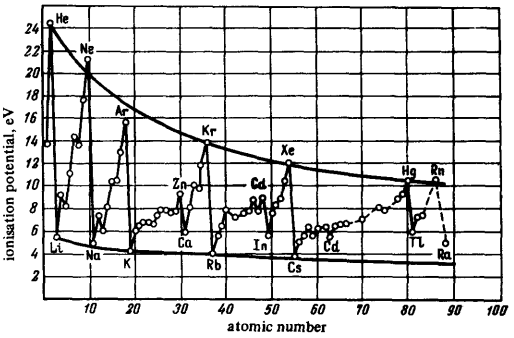

Figure 4. Ionisation potentials of the elements (for the first electron).

In each period of Mendeleev's system the highest ionisation potential corresponds to an inert gas, and the lowest to an alkali metal. With these and with other extreme elements the ionisation potentials diminish with increase in the atomic number, this undoubtedly being due to the increase in atomic radius resulting from the filling of increasingly remote electron shells of the atom. It is also significant that the difference between the ionisation potentials of the inert gas and the alkali metal shrinks considerably on passing to the end of the Periodic System. This explains the enhanced chemical activity of the heavy inert gases—xenon and radon—and also the ability of the near and intermediate actinides to exhibit a high and variable valency. It may be supposed that the far actinides will also give compounds of high valency, although under normal conditions their most characteristic valencies are 3 and 2.

The valency of element No. 104, kurchatovium, is of great interest. This element is not an actinide, but should be analogous to hafnium and quadrivalent. Zvara and coworkers[7] at the Joint Institute for Nuclear Research (in Dubna) used an elegant method to show that the valency of kurchatovium actually differs from that of the lanthanides and the far actinides (Fig. 5). The products of the nuclear reaction leading to the formation of $^{260}_{104}$Ku nuclei were carried away by a stream of nitrogen and chlorine with the addition of hafnium tetrachloride and niobium pentachloride through a special filter, which at 350°C retained the less volatile chlorides of the lanthanides and elements 101–103. After this the spontaneous fission counters detected element No. 104 as before, which indicates that it differs from the lanthanides and the actinides.

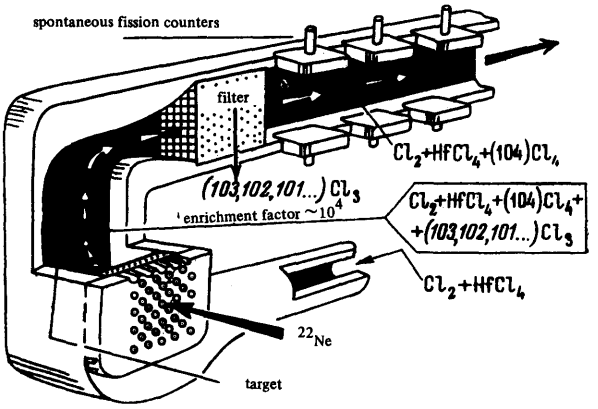

Figure 5. Diagram of apparatus for determining the valency state of element No. 104.

Formally element No. 105 should be an analogue of tantalum, element No. 106 of tungsten, and so on. However, in view of the energetic similarity of 5*f*- and 6*d*-electrons, the nearer transactinides (having $Z = 104$–106) may be expected to exhibit also an anomalous high valency, similarly to elements of the copper subgroup, where the higher valency is due to the closeness of the energy levels of the *d*- and outer *s*-electrons.

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A valuable contribution to the Periodic System has been made by a study of the chemical properties of Group 0 elements. During the 1930s B. A. Nikitin showed, using a method of cocrystallisation with sulphur dioxide hydrate $SO_2.6H_2O$, that radon and certain other inert gases form the hexahydrates $Rn.6H_2O$, $Ar.6H_2O$, $Ne.6H_2O$, etc. Later he found that radon interacts also with toluene, *p*-chlorophenol, and other organic compounds to yield the coordination compounds $Rn.2C_6H_5CH_3$, $Rn.3ClC_6H_4OH$.

The first compound of the inert gas xenon formed by means of a valency bond was obtained in 1962 by N. Bartlett, who found that platinum hexafluoride PtF_6, an extremely strong oxidant, was able to oxidise xenon to a compound having the formula $Xe^+(PtF_6)^-$. This is hydrolysed by water:

$$2XePtF_6 + 6H_2O = 2Xe + O_2 + 3PtO_2 + 12HF \ .$$

After this discovery other workers obtained the fluoride XeF_4 by the direct interaction of fluorine and xenon at 400°C followed by rapid cooling to room temperature. Xenon tetrafluoride is stable at ordinary temperatures. It is hydrolysed by water:

$$XeF_4 + 2H_2O = Xe + O_2 + 4HF \ .$$

Ultraviolet irradiation of a mixture of xenon and fluorine yields the difluoride XeF_2. With excess of fluorine at

high pressures (60–70 atm) the hexafluoride XeF_6 is also formed. On hydrolysis by water this compound forms a non-volatile solid product, which has proved to be xenon trioxide XeO_3. This solid is stable in light and air, but deliquesces in the presence of moisture. When heated, xenon trioxide explodes. It can also undergo disproportionation, with the formation of a tetroxide:

$$4XeO_3 = 3XeO_4 + Xe$$

The salts $CsHXeO_4$, $BaXeO_4$, termed *xenonates*, correspond to xenon trioxide, and *perxenonates* ($Na_4XeO_6.8H_2O$, $K_4XeO_6.9H_2O$, etc.) to xenon tetroxide.

The simple compounds of xenon known at the present time are listed below:

Valency			
2	4	6	8
XeF_2 $XeCl_2$ XeO	XeF_4 XeF_2 XeO_2	XeF_6 XeF_4 XeO_3F_2 XeO_3	(XeF_8) XeO_4

Xenon fluorides are white crystalline substances, which decompose when heated. They possess strong oxidising properties: for example, a mixture of the tetrafluoride and the hexafluoride ignites methanol and aqueous ammonia, and converts bivalent manganese into permanganic acid. Perbromates were first prepared by means of xenon fluorides.

Radon has been found to react with fluorine. Chemical compounds of radon will probably be more stable than those of the other inert gases. However, the strong radioactivity of this element makes study of its chemistry difficult. Only one compound of krypton KrF_2 has been obtained, and it is not very stable at ordinary temperatures. On theoretical grounds the formation of chemical compounds by argon, neon, and helium is improbable.

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The physical and chemical properties of elements and their compounds already began to be compared with the position of the corresponding elements in the Periodic System during the first few decades after the discovery of the Periodic Law. Increasing attention has recently been paid to the search for quantitative relations in this field. The following papers may be cited as examples.

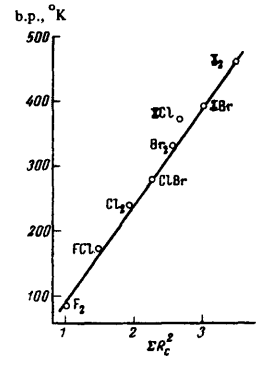

Figure 6. Dependence of boiling points of diatomic interhalogen compounds on covalent radii of halogen atoms.

G.R. Somayajulu and S.R. Palit (1957) studied the relation between the boiling point of various halogen derivatives and the dimensions of the atoms they contained. It was found that the boiling point of members of a given series of halogen derivatives, e.g. interhalogen compounds, was a linear function of the surface area of the halogen atoms calculated for the given molecule. The boiling point can be calculated by means of the formula $T_b = a\Sigma R_c^2 + b$, where T_b (°K) is the boiling point, R_c are the covalent radii of the halogen atoms in the molecule, and a and b are constants.

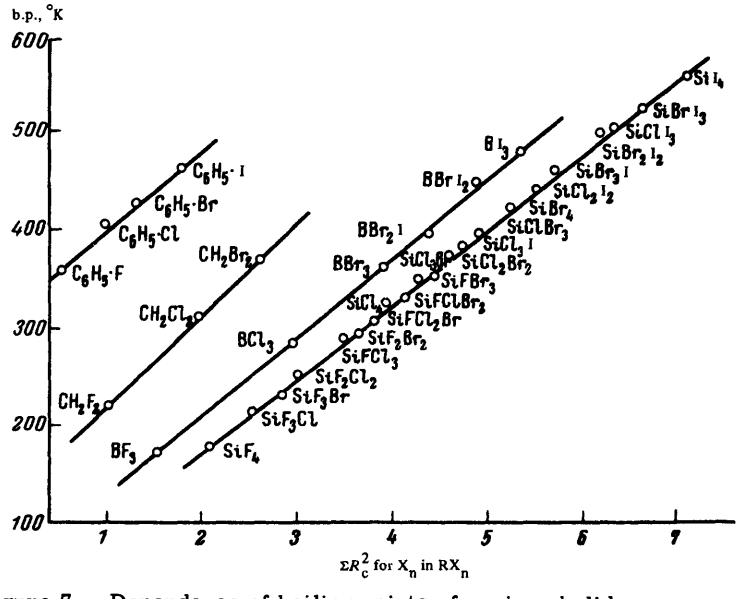

Figure 7. Dependence of boiling points of various halides on covalent radii of halogen atoms.

Fig. 6 shows the applicability of this formula to determining the boiling points of interhalogen compounds of the type X_2, and Fig. 7 those of four series of halogen derivatives of various types.

Z. Szabo and B. Lakatos (1952) put forward the view that the physical properties of uncombined elements (their melting and boiling points, heats of sublimation) depend not only on the atomic numbers but also on the fine distribution of electrons among s-, p-, and d-sublevels.

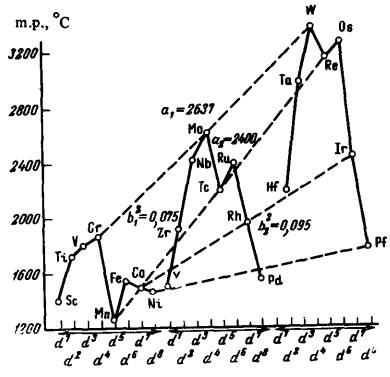

Figure 8. Melting points of the transition elements.

This leads to additional periodicity within each period of Mendeleev's system. Fig. 8 illustrates this phenomenon for the melting points of the transition metals in three long periods. Points representing the melting points of analogous elements usually lie on straight lines. To calculate the melting points of elements these workers proposed the equation

$$T = a_1 e^{-b_1^2(d-4)^2} + a' e^{-b'^2(d-5)^2}(n - n_5), \quad \text{if} \quad d \leqslant 5$$

or

$$T = a_2 e^{-b_2^2(d-6)^2} + a' e^{-b''^2(d-5)^2}(n - n_5), \quad \text{if} \quad d > 5$$

where T is the melting point, a_1, a_2, b_1, and b_2 are constants of the periodic curve, a', b', and b'' are constants in the function representing the slope of the curve, n is the principal quantum number, and d is the number of d-electrons if the whole calculation is derived from the properties of elements in the fifth period (n_5). The average difference between calculated and experimental values was 4%.

An. N. Nesmeyanov and N. E. Khandamirova (1960) found quantitative relations between the heats of sublimation of elements ΔH°_{298} and their positions in the Periodic System. Regarding the lattice energy of a solid as a function of two main variables—the interatomic distance r and the atomic weight A—these workers established that the quantity $\Delta H^\circ_{298} A/r$ is a linear function of the atomic weight within each subgroup of the Periodic System. Heats of sublimation can be calculated from the appropriate graphs. In most cases satisfactory agreement is found between calculated and experimental values. Deviation is observed in the copper and zinc subgroups, which is explained by penetration of s-electrons below the screen of d-electrons and the resultant relative decrease in size of the atoms.

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The centenary of the Periodic Law has revealed the whole multiplicity of its applications in chemistry, physics, and several related fields of knowledge. It has not only explained many known facts, but has enabled new, frequently unexpected phenomena to be predicted. However, the successes achieved do not mean that the possibilities of the Periodic Law are exhausted. As a guiding light it will always indicate to researchers the path to new discoveries, while the name of its author, the great Russian scientist Dmitrii Mendeleev, has been introduced forever into the golden tables of modern science.

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The Application of the Hammett Equation with the Constants σ^{ph} in the Chemistry of Organophosphorus Compounds

T.A.Mastryukova and M.I.Kabachnik

The review deals with the application of the Hammett equation to organophosphorus reactions and equilibria using the constants σ^{ph}. As far as possible a complete list of the constants σ^{ph} is given. Analysis of the application of the constants σ^{ph} shows that linear correlations between the rate and equilibrium constants for organophosphorus reactions are usually obtained when the phosphorus atom is not a reaction centre.
For reactions involving phosphorus directly, linear correlations are achieved with the aid of the inductive (σ_I^{ph}) and resonance (σ_R^{ph}) constants, namely: $\Sigma(\sigma_I^{ph} + \alpha\sigma_R^{ph})$. A method of calculation of the constants σ_I^{ph} and σ_R^{ph} is described and as far as possible a complete list of these constants is given for various groups attached to the phosphorus atom.
It has been demonstrated on 124 reaction series as examples the function $\Sigma(\sigma_I^{ph} + \alpha\sigma_R^{ph})$ makes it possible to construct a universal system for the $\sigma\rho$ analysis of reactions, equilibria, and certain physical constants in the chemistry of organophosphorus compounds on the basis of the equation $\lg K = \lg K^0 + \rho\Sigma(\sigma_I^{ph} + \alpha\sigma_R^{ph})$ with high correlation coefficients.
The relation between the constants α and ρ on the one hand and the type of reaction and its mechanism on the other is discussed.
The bibliography includes 117 references.

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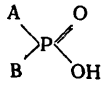
1. INTRODUCTION

A characteristic feature of studies on the reactivity of organophosphorus compounds in recent years consists in the measurement of a large number of rate and equilibrium constants and the application of correlation equations to them. The first Hammett equation[1]:

$$\log \frac{K}{K^0} = \rho\sigma \qquad (1)$$

with the constants σ_p and σ_m^2 was applied to organophosphorus compounds in 1953 by Jaffé et al.[3] for the ionisation of aromatic phosphonic acids. In 1956 Kabachnik[4] showed that the Hammett equation is applicable to a wide variety of phosphorus acids:



and not only to aromatic acids provided that one uses the constants σ^{ph} specific to substituents linked to the phosphorus atom:

$$pK = pK^0 - \rho\Sigma\sigma^{\Phi}. \qquad (2)$$

In order to determine the constants σ^{ph}, about 150 ionisation constants of phosphorus acids in water and in 50% aqueous alcohol were employed in the calculation and the first 57 constants σ^{ph} were obtained. The use of these constants resulted in entirely satisfactory correlations between the ionisation constants (pK_a) of the acids (Table 2, series No. 1, 5, 12, 13).

2. THE CONSTANTS σ^{ph} FOR SUBSTITUENTS AT THE PHOSPHORUS ATOM

In recent years numerous quantitative data have accumulated on equilibrium and rate constants for reactions of organophosphorus compounds. Part of these data were used to determine new constants σ^{ph}. Thus, Kabachnik, Mastryukova, Melent'eva, and Shipov[5-7] determined the constants σ^{ph} for the C_6H_5O, p-$CH_3C_6H_4O$, cyclo-C_5H_9, and $CH_2{=}CH$ groups and Kabachnik, Balueva, and coworkers[8,9] determined the constants for the cyclo-C_6H_{11}, $NC{-}CH_2CH_2$, and $C_6H_{13}O$ groups. Ryss and Tul'chinksii[10] determined the constants σ^{ph} for fluorine directly linked to phosphorus, etc. However, the majority of the quantitative data have not been interpreted from this standpoint although their use would permit the determination of many new values of σ^{ph}.

Column 3 of Table 1 gives a complete compilation of the constants σ^{ph} published previously and calculated by the present authors from the literature data. Many of these constants were obtained as averages from several measurements in different reaction media and were then successfully used in various correlations. These constants are fairly reliable and have been printed in bold type in Table 1. The less reliable constants are printed in the usual type; the least reliable values are quoted with only one figure after the decimal point.

3. CORRELATIONS BETWEEN THE EQUILIBRIUM AND RATE CONSTANTS FOR REACTIONS AND THE CONSTANTS σ^{ph}

The constants σ^{ph} were found to be applicable in all those cases where the reaction does not involve directly the phosphorus atom, i.e. when the phosphorus atom is not subject to direct attack and hence σ-bonds involving phosphorus are not dissociated and new ones are not formed.

Table 1. The constants σ*, σ^{ph}, σ_I^{ph}, and σ_R^{ph} for substituents.

R	σ*	σ^{ph}	σ_I^{ph}	σ_R^{ph}	References	
					σ*	σ^{ph}
1	2	3	4	5	6	7
H	0.49	0	0	0	11	4
CH_3	0	−0.96	−0.96	0	11	4
C_2H_5	−0.100	−0.10	−1.10	0	11	4
C_3H_7	−0.115	−1.18	−1.18	0	11	4
iso-C_3H_7	−0.190	−1.30	−1.30	0	11	4
C_4H_9	−0.130	−1.22	−1.22	0	11	4
iso-C_4H_9	−0.125	−1.30	−1.30	0	11	4
s-C_4H_9	−0.210	−1.36	−1.36	0	11	4
t-C_4H_9	−0.300	−1.55	−1.55	0	11	4
C_5H_{11}	−0.162	−1.21	−1.21	0	11	12*
iso-C_5H_{11}	−0.162	−1.27	−1.27	0	11	12*
neo-C_5H_{11}	−0.165	−1.44	−1.44	0	11	13*
t-C_5H_{11}		−1.54	−1.54	0		13*
C_6H_{13}		−1.21	−1.21	0		12*
		−1.19	−1.19	0		13*
iso-C_6H_{13}		−1.21	−1.21	0		12*
C_8H_{17}		−1.11	−1.11	0		8
$C_{12}H_{25}$		−1.24	−1.24	0		13*
cyclo-C_5H_9	−0.200	−1.25	−1.25	0	11	6
cyclo-C_6H_{11}	−0.17	−1.19	−1.19	0	14	8
$CH_2{=}CH$	0.59	−0.68	0.22	−0.90	15	16
$CH_2{=}CH{-}CH_2$	0.23	−0.83	−0.50	−0.33	15*	13*
$C_6H_5CH_2$	0.215	−0.69	−0.53	−0.16	11	13*
$C_6H_5CH_2CH_2$	0.08	−1.06	−0.80	−0.26	11	17*
$(C_6H_5)_2CH$	0.405	−0.73	−0.15	−0.58	11	17*
$(C_6H_5)_3C$		−1.02				13*
$C_6H_5CH{=}CH$	0.41	−0.58	−0.14	−0.44	11	13*
$C_6H_5C{\equiv}C$	1.35	0.28	1.72	−1.44	11	17*
$HOCH_2$	0.555	−0.55	0.14	−0.69	11	4
$ClCH_2$	1.05	−0.05	1.13	−1.18	11	18
$BrCH_2$	1.00	0.0	1.0	−1.0	11	4
ICH_2	0.85	−0.1	0.7	−0.8	11	4
$C_6H_5OCH_2$	0.85	−0.2	0.7	−0.9	11	17*
$(CH_3)_3SiCH_2$	−0.26	−1.6	−1.5	−0.1	11	13*
Cl_2CH	1.94	0.27	2.90	−2.63	11	4
Cl_3C	2.61	0.3	4.2	−3.9	15	4
F_3C	2.49	0.7	4.0	−3.3	15	4[a]
$BrCH_2CH_2$	0.26	−0.8	−0.4	−0.4	11	13*
	0.40	−0.8	−0.2	−0.6	15	13*
$C_6H_5OCH_2CH_2$	0.27	−0.77	−0.42	−0.35	15*	12*
$NCCH_2CH_2$	0.80	−0.6	0.6	−1.2	11	8
	0.49	−0.6	0.0	−0.6	15*	8
$ClCH_2CH_2CH_2$	0.16	−0.72	−0.65	−0.07	15*	12*
^{-}O		0				4
HO	1.31	−0.39	1.65	−2.04	15	4
CH_3O	1.73	−0.12	2.48	−2.61	19*	4
C_2H_5O	1.64	−0.21	2.30	−2.52	19*, 20*	4
C_3H_7O	1.57	−0.32	2.16	−2.48	19*, 20*	4
iso-C_3H_7O	1.51	−0.29	2.04	−2.34	19*, 20*	4
C_4H_9O	1.55	−0.41	2.13	−2.54	19*, 20*	4
iso-C_4H_9O	1.52	−0.30	2.06	−2.36	19*, 20*	4
$C_5H_{11}O$	1.52	−0.39	2.06	−2.45		21*
iso-$C_5H_{11}O$	1.52	−0.38	2.06	−2.45		22*
neo-$C_5H_{11}O$	1.51	−0.29	2.04	−2.33		21
$C_6H_{13}O$		−0.32				9
	1.51	−0.40	2.04	−2.44		21*
$(CH_3)_2C{-}CH(CH_3)O$	1.46	−0.5	1.95	−2.45		21; σ_R^{ph} 23*
$ClCH_2CH_2O$		0.03			from σ^{ph} and σ_R^{ph}	9*
cyclo-$C_6H_{11}O$		−0.35				24*
C_6H_5O	2.24				15	
	1.91[b]	−0.06	2.83	−2.89		5
p-$CH_3C_6H_4O$		−0.14				5
CH_3S	1.47	0.15	1.96	−1.81	25*	26*
C_2H_5S	1.44	0.09	1.90	−1.81	27*	26*, 28*
C_3H_7S	1.38	−0.06	1.78	−1.84	27*	26*
iso-C_3H_7S	1.47	−0.06	1.96	−2.02	27*	26*
$(CH_3)_2N$	0.62	−1.22	0.27	−1.49	29*	30*
$(C_2H_5)_2N$	0.39	−1.54	−0.18	−1.36		31*, σ_R^{ph} 32*
p-$CH_3C_6H_4NH$		−1.7				33*
F	3.10	0.56	5.21	−4.65	15	10
Cl	2.68	0.93	4.37	−3.44	15	9*
C_6H_5	0.62	−0.48	0.27	−0.76	15	4
		−0.59[c]				6
C_6F_5	4.07	−0.02	7.13	−7.15	39*	39*

Table 1 (continued)

Aromatic Groups

R	σ^{ph}	Refs.	R	σ^{ph}	Refs.
m-$CH_3\overset{+}{N}H_2C_6H_4$	0.3	4	p-$CH_3C_6H_4$	−0.60	4
				−0.72[c]	16
p-$(CH_3)_2\overset{+}{N}HC_6H_4$	0.3	4	m-$C_6H_5NHC_6H_4$	−0.62	4
			p-HOC_6H_4	−0.65	4
m-$C_6H_5\overset{+}{N}H_2C_6H_4$	0.3	4	m-$CH_3NHC_6H_4$	−0.65	4
p-$NO_2C_6H_4$	0.13	4	p-$C_6H_5OC_6H_4$	−0.66	4
m-$NO_2C_6H_4$	0.10	4	m-$C_6H_5NHC_6H_4$	−0.67	4
p-$NH_2SO_2C_6H_4$	0.00	4	p-$(CH_3)_2NC_6H_4$	−0.68	4
p-CNC_6H_4	−0.04	34*		−0.91	41*
p-$HOCOC_6H_4$	−0.14	4		−1.17[c]	38*
m-$HOCOC_6H_4$	−0.18	4	p-$NH_2C_6H_4$	−0.78	4
m-ClC_6H_4	−0.22	4	p-$NH_2NHC_6H_4$	−0.79	4
m-BrC_6H_4	−0.23	4	p-$CH_3NHC_6H_4$	−0.81	4
p-$CH_3OCOC_6H_4$	−0.24	35*	p, m-$CH_2O_2C_6H_3$	−0.55	4
p-BrC_6H_4	−0.25	4	p-$C_6H_5COOC_6H_4$	−0.02	40*
p-ClC_6H_4	−0.29	4			
m-HOC_6H_4	−0.32	4			
m-$^{-}OCOC_6H_4$	−0.42	4			
p-$^{-}OCOC_6H_4$	−0.42	4			
m-$CH_3OC_6H_4$	−0.45[c]	36*, 37			
m-$NH_2NHC_6H_4$	−0.46	4			
p-$CH_3CONHC_6H_4$	−0.49	4			
p-$C_6H_5SC_6H_4$	−0.50	4			
m-$CH_3C_6H_4$	−0.55[c]	37*			
m-$NH_2C_6H_4$	−0.56	4			
p-$CH_3OC_6H_4$	−0.59	4			
	−0.74[c]	16			

[a] There was a misprint in the original: 0.50 was printed instead of 0.7 for σ^{ph}.
[b] Derived as the mean from numerous correlations for reactions of organophosphorus compounds.
[c] For two and more aryl groups at the phosphorus atom.
*Studies the data from which we employed in the calculation of the corresponding values of σ are denoted by an asterisk.

Table 2 presents the results for the correlations between the ionisation constants (pK_a) of organophosphorus acids in various media. Evidently the ionisation constants of acids of different types—phosphoric and phosphonic (first and second ionisations), phosphinic, phosphonous, and thioic, selenoic, and dithioic phosphorus acids—as well as the ionisation constants for phosphonium salts treated as acids show a satisfactory linear correlation with $\Sigma\sigma^{ph}$ regardless of the nature of the groups attached to phosphorus: alkyl and cycloalkyl groups, alkyl groups with electronegative substituents, aryl groups with different substituents, and also alkoxy-, aryloxy-, and other groups (see Figs. 1–3). It should be noted that such universal correlation is not always observed with other σ constants (σ*, σ^0, σ_p, σ_m, etc.). Whereas a satisfactory correlation is observed with the constants σ* for alkyl substituents[51] and the constants σ^0 [51] and σ [52] for aryl substituents, alkoxy-substituents remain outside the correlations. Here, of course, a unique correlation is not attainable.

Many of the acid ionisation constants listed in Table 2 are due to the authors of the review and others were taken from the literature. They were correlated in most cases by the present authors.

Table 3 presents the correlation of the protolysis constants (pK_p) of phosphorus acids in non-aqueous media using Hexamethoxy-Red as the base indicator.

Table 4 shows the relation between the basicity constants (pK_a) of phosphines, phosphine oxides, iminophosphoranes, and other substances and the constants σ^{ph}.

Table 2. Correlation of the ionisation constants of phosphorus acids in aqueous alcohol with the constants σ^{ph} ($pK = pK^0 - \rho\Sigma\sigma^{ph}$; $\alpha = 1.00$).

No. of series	Acid	Temp., °C	Alcohol content, %	No. of points n	pK_a^0	$\rho \pm S_\rho$	r	Standard deviation S	Refs.
1	ABPOOH		0	58	1.00	0.99±0.03	0.976		4
2	ABPOOH	20	0	8	0.98	1.06±0.12	0.965	0.27	42*
3	ABPOOH	20	0	5	1.05	0.95±0.10	0.982	0.21	43*
4	ABPOOH	20	7	20	1.02	1.04±0.02	0.995	0.07	44
5	ABPOOH		50	17	2.01	1.31±0.04	0.993		4
6	ABPOOH	20	50	16	2.05	1.24±0.03	0.995	0.07	44
7	ABPOOH	22	75	19	2.41	1.49±0.12	0.950	0.30	24*
8	ABPOOH	20	80	23	2.70	1.22±0.03	0.993	0.03	44
9	ABPOOH	22	95	17[a]	2.90	1.58±0.14	0.953	0.33	24*
10	ABPOOH	20	100	6[b]	6.70	0.91±0.09	0.982	0.15	43*
11	Ar_2POOH	23	THF 60	10	2.17	1.49±0.05	0.995	0.05	45*
12	AP (O) (O^-) OH		0	47	6.13	1.79±0.08	0.955		4
13	AP (O) (O^-) OH		50	19	7.59	1.36±0.04	0.992		4
14	ArP (H) OOH	25	0	6	1.14	1.20±0.14	0.974	0.06	34*
15	ABPSOH	20	7	8	0.70	0.92±0.02	0.995	0.07	46
16	ABPSOH	20	80	23	2.06	1.31±0.02	0.995	0.06	46
17	ABPSOH	20	100	5	6.79	0.70±0.10	0.945	0.10	43*
18	ABPSeOH	20	7	6	0.56	0.88±0.02	0.999	0.03	47
19	ABPSeOH	20	80	6	1.77	1.34±0.03	0.992	0.11	47
20	ABPSSH	20	7	17	1.74	−0.01±0.05	0.978[c]	0.12	48*
21	ABPSSH	20	80	17	2.64	−0.02±0.03	0.994[c]	0.06	48*
22	p-ABP(O)C_6H_4COOH	25	50	6	4.88	0.02±0.01	0.999[c]	0.02	49*
23	m-ABP(O)C_6H_4COOH	25	50	5	5.05	0.04±0.01	0.999[c]	0.02	49*
24	$[Ar_3\overset{+}{P}$--$CH_2COC_6H_5]$ X^-[d]	20	50	5	3.29	1.79±0.19	0.983	0.12	36*
25	$[Ar_3\overset{+}{P}$—$CH_2COC_6H_5]$ X^-[d]	20	80	6	3.27	1.58±0.16	0.979	0.17	36*
26	$[R_3\overset{+}{P}$—$CH_2COC_6H_5]$ X^-[d]	20	95	4	2.54	2.11±0.11	0.997	0.12	50*
27	$\left[Ar_3\overset{+}{P}-CH(C_6H_4\text{-}o)(C_6H_4\text{-}o)\right]Br^-$		95	9	6.22	2.02±0.21	0.964	0.23	37*

[a] The point corresponding to $(C_6H_5O)_2POOH$ was excluded.
[b] The points corresponding to $(ArO)_2POOH$ and $(ClCH_2)(ArO)POOH$ were excluded.
[c] The correlation coefficient was calculated after rotating the coordinate axes by 45°.
[d] X = Cl or Br.
*Studies the data from which were used for the correlations.

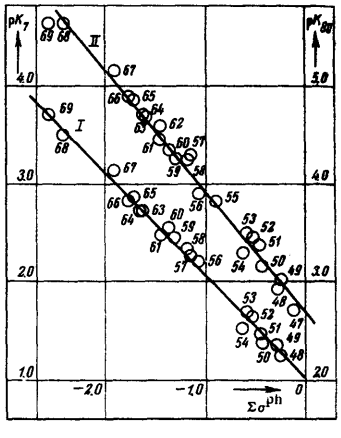


Figure 1. Variation of the ionisation constants (pK_a) of phosphorus acids of the type ABPOOH with $\Sigma\sigma^{ph}$ in 7% (I) and 80% (II) aqueous alcohol (see Table 2, series 4 and 8). The numbers of the points and the substituents A and B for the acids are indicated: 47) C_6H_5O, C_6H_5O; 48) CH_3O, CH_3O; 49) p-$CH_3C_6H_4O$, p-$CH_3C_6H_4O$; 50) C_2H_5O, C_2H_5O; 51) C_6H_5O, OH; 52) p-$CH_3C_6H_4O$, OH; 53) p-ClC_6H_4, p-ClC_6H_4; 54) C_3H_7O, C_3H_7O; 55) CH_2=CH, C_2H_5O; 56) CH_2=CH, OH; 57) CH_2=CH, C_6H_5; 58) C_6H_5, C_6H_5; 59) C_6H_5, p-$CH_3C_6H_4$; 60) CH_2=CH, CH_2=CH; 61) p-$CH_3C_6H_4$, p-$CH_3C_6H_4$; 62) p-$CH_3OC_6H_4$, p-$CH_3OC_6H_4$; 63) cyclo-C_5H_9, OH; 64) C_3H_7, C_6H_5; 65) cyclo-C_5H_9, C_6H_5; 66) iso-C_3H_7, C_6H_5; 67) CH_3, CH_3; 68) C_4H_9, C_4H_9; 69) iso-C_4H_9, iso-C_4H_9.

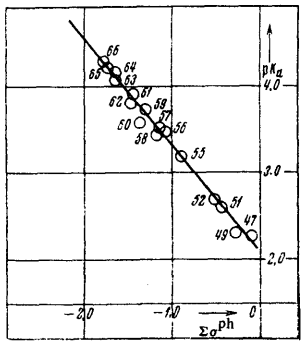


Figure 2. Variation of the ionisation constants (pK_a) of phosphorus acids of the type ABPOOH with $\Sigma\sigma^{ph}$ in 50% aqueous alcohol (see Table 2, series 6; the legend is the same as in Fig. 1).

These data were obtained mainly in nitromethane and are due to different investigators. Here too satisfactory correlation coefficients have been obtained (see also Figs. 4 and 5).

The attempt by Henderson and Streuli[61] to correlate the pK_a for phosphines with the inductive constants σ^* should be noted. They obtained a pronounced scatter of points which they interpreted as three parallel straight lines with relatively satisfactory correlation for primary, secondary,

and tertiary phosphines. When the constants σ^{ph} are employed, a single correlation is achieved for phosphines of all types with a better correlation coefficient.

Table 5 presents the correlations between the rate constants for certain reactions of organophosphorus compounds. These are alkylation of salts of dithioic phosphorus acids with benzyl chloride, bromination of the double bonds in vinyl derivatives of phosphorus, Pishchimuka rearrangement, etc. (Figs. 6 and 7). It should be noted that unfortunately the reaction mechanisms have not always been established[65], which makes $\sigma\rho$ analysis difficult.

Nikolaev et al.[66] showed that the constants σ^{ph} are applicable to the correlation of the quantitative data on the extraction of actinide salts by organophosphorus extracting agents from nitric acid media into organic solvents. It was found that linear correlations hold not only for the effective extraction constants ($\bar{k}$) or the stability constants of the complexes but also for the partition coefficients (K_p); the relevant data are presented in Table 6.

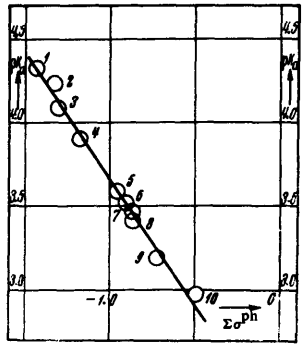


Figure 3. Variation of the ionisation constants (pK_a) of phosphorus acids of the type Ar_2POOH with $\Sigma\sigma^{ph}$ in 60% aqueous tetrahydrofuran (see Table 2, series 11): 1) p-$CH_3C_6H_4$, p-$CH_3C_6H_4$; 2) p-$CH_3OC_6H_4$, C_6H_5; 3) p-$CH_3C_6H_4$, C_6H_5; 4) C_6H_5, C_6H_5; 5) p-ClC_6H_4, C_6H_5; 6) p-BrC_6H_4, C_6H_5; 7) m-BrC_6H_4, C_6H_5; 8) m-ClC_6H_4, C_6H_5; 9) p-ClC_6H_4, p-ClC_6H_4; 10) p-$NO_2C_6H_4$, C_6H_5.

Table 3. Correlation of the protolysis constants for phosphorus acids at 20°C in non-aqueous media using Hexamethoxy-Red as the indicator base ($pK_p = pK_p^0 - \rho\Sigma\sigma^{ph}$; $\alpha = 1.00$).

No. of series	Acid	Medium	n	pK_p^0	$\rho \pm S_\rho$	r	S	Refs.
1	ABPOOH	C_6H_6	4	−2.89	6.11±0.08	0.982	0.19	18
2	ABPOOH	C_6H_5Cl	4	−3.51	7.02±0.05	0.994	0.12	18
3	ABPSOH	C_6H_6	7	−2.12	1.00±0.05	0.994	0.05	18
4	ABPSOH	C_6H_5Cl	7	−2.53	1.06±0.04	0.997	0.04	18
5	ABPSSH	C_6H_6	4	−1.29	0.89±0.08	0.992	0.05	18
6	ABPSSH	C_6H_5Cl	4	−2.20	0.96±0.07	0.990	0.05	18

*Studies the data from which were used for the correlations.

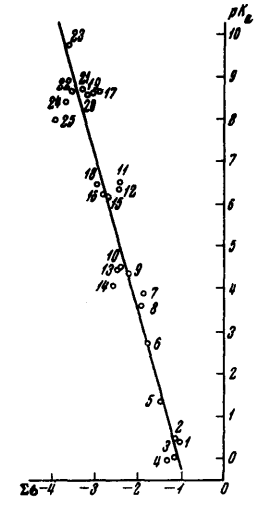


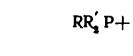
Figure 4. Variation of the basicity constants (pK_a) of phosphines of the type $R'R''R'''P$ with $\Sigma\sigma^{ph}$ in nitromethane (see Table 4, series 3): 1) $CNCH_2CH_2$, $CHCH_2CH_2$, H; 2) C_8H_{17}, H, H; 3) C_6H_5, C_6H_5, H; 4) iso-C_4H_9, H, H; 5) $CNCH_2CH_2$, $CNCH_2CH_2$, $CNCH_2CH_2$; 6) C_6H_5, C_6H_5, C_6H_5; 7) CH_3, CH_3, H; 8) CH_3, $CNCH_2CH_2$, $CNCH_2CH_2$; 9) C_8H_{17}, C_8H_{17}, H; 10) cyclo-C_6H_{11}, cyclo-C_6H_{11}, H; 11) CH_3, CH_3, C_6H_5; 12) CH_3, CH_3, $CNCH_2CH_2$; 13) C_4H_9, C_4H_9, H; 14) iso-C_4H_9, iso-C_4H_9, H; 15) C_2H_5, C_2H_5, C_6H_5; 16) C_8H_{17}, C_8H_{17}, $CNCH_2CH_2$; 17) CH_3, CH_3, CH_3; 18) C_4H_9, C_4H_9, $CNCH_2CH_2$; 19) CH_3, CH_3, C_2H_5; 20) C_2H_5, C_2H_5, CH_3; 21) C_2H_5, C_2H_5, C_2H_5; 22) C_3H_7, C_3H_7, C_3H_7; 23) cyclo-C_6H_{11}, cyclo-C_6H_{11}, cyclo-C_6H_{11}; 24) C_4H_9, C_4H_9, C_4H_9; 25) iso-C_4H_9, iso-C_4H_9, iso-C_4H_9.

Table 4. Correlation of the basicity constants (pK_a) of organophosphorus bases with the constants σ^{ph} ($pK_a = pK_a^0 - \rho\Sigma\sigma^{ph}$; $\alpha = 1.00$).

No. of series	Formula	Medium	n	pK_a^0	$\rho \pm S_\rho$	r	S	Refs.
1	Ar_3P, 20°	80% C_2H_5OH	6[a]	0.26	1.90±0.25	0.968	0.12	53*
2	R_3P	C_2H_5OH	10	0.93	2.11±0.56	0.802	1.05	54*
3	R_3P	CH_3NO_2	25	−3.45	3.42	0.950		8
4	$XC_6H_4P(C_6H_5)_2$	CH_3NO_2	6	4.23	4.61±0.26	0.994	0.14	41*
5	R_3PO	CH_3NO_2	7	2.40	1.69±0.19	0.970	0.22	35*
6	$R_2P(O)—CH_2—P(O)R_2$	CH_3NO_2	10	4.59	0.79±0.22	0.985	0.25	55
7	$Ar_3P{=}NC_6H_5$	95% C_2H_5OH	4	2.82	3.41±0.12	0.989	0.25	56*
8	$ABCP{=}NC_6H_5$	CH_3NO_2	9	13.17	1.90±0.13	0.981	0.24	57
9	$ABCP{=}NC_6H_4F$-p	CH_3NO_2	8	12.78	1.89±0.15	0.982	0.26	57
10	$XC_6H_4P(C_6H_5)_2{=}NC_6H_4NO_2$-$p$	CH_3NO_2	6	14.34	2.49±0.16	0.992	0.12	58*
11	ABP (=NR) (NHR')	CH_3NO_2	10	13.02	1.68	0.981	0.30	59
12	cyclo-$(R_2PN)_3$	CH_3NO_2	10	2.49	1.24±0.11	0.971	0.97	60*

[a] The point corresponding to $(p\text{-}ClC_6H_4)_3P$ was excluded (see Ref. 53).
*Studies the data from which were used for the correlations.

Table 5. Correlation of the rate and equilibrium constants for certain reactions of organophosphorus compounds with the constants σ^{ph} ($\lg K = \lg K^0 - \rho\Sigma\sigma^{ph}$; $\alpha = 1.00$).

No. of series	Reaction	Temp., °C	Medium	n	$\lg K^0$	$\rho \pm S_\rho$	r	S	Refs.
1	ABPSSNA+$C_6H_5CH_2Cl$	25	96% C_2H_5OH	12	−3.87	−0.236	0.964		48
2	ABP (S) OC_2H_5+C_3H_7I	105	C_3H_7I	6	−5.53	−0.40±0.02	0.995	0.05	33*
3	ABP (=NC_6H_5) OC_2H_5+C_2H_5I	50	CH_3CN	6	−3.44	−0.60±0.06	0.984	0.08	62
4	RR'_2P+ 	35	C_6H_6	5	−4.13	−1.78±0.62	0.856	0.23	63*
5	ditto	40	C_6H_6	4	−4.35	−2.45±0.65	0.935	0.19	63*
6	»	45	C_6H_6	4	−4.23	−2.42±0.80	0.907	0.23	63*
7	$Ar_3P+N_3C_6H_5 \underset{k_2}{\overset{k_1}{\rightleftarrows}} Ar_3P{=}N{-}N{=}NC_6H_5$	25	C_6H_6	5	−2.64	−1.01±0.24	0.922	0.15	38*
8		25	C_6H_6	5	−1.06	0.38±0.06	0.969	0.03	38*
9	$Ar_3PN_3C_6H_5 \xrightarrow{k_3} Ar_3P{=}NC_6H_5+N_2$	25	C_6H_6	5	−1.07	0.40±0.15	0.838	0.09	38*
10	Ar_3P+S	25	C_6H_6	5	−7.09	−2.71±0.19	0.992	0.17	64*
11	ABP (O) $CH{=}CH_2+Br_2$, $k_{1/2}$	15	CCl_4	14	−3.38	−0.78±0.07	0.950	0.12	9
12	$Ar_3P{=}NC_6H_5+C_6H_5CHO$	45.5	C_2H_5OH	4	−0.79	−0.24±0.04	0.976	0.03	56*
13	ABP (S) OH ⇄ ABP (O) SH	20	7% C_2H_5OH	9	0.80	1.32±0.13	0.964	0.13	46
14	ABP (S) OH ⇄ ABP (O) SH	20	80% C_2H_5OH	7	0.90	2.51±0.38	0.947	0.17	46

*Studies the data from which were used for the correlations.

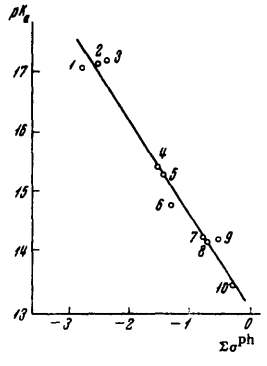


Figure 5. Variation of the basicity constants (pK_a) of phosphamidines of the type ABP(=NR)NHR′ with $\Sigma\sigma^{ph}$ in nitromethane (see Table 4, series 11). The numbers of the points and the substituents A and B are indicated for constant R = p-$CF_3C_6H_4$ and R′ = p-$CH_3OC_6H_4$: 1) iso-C_4H_9, iso-C_4H_9; 2) C_3H_7, C_3H_7; 3) C_2H_5, C_2H_5; 4) C_2H_5, iso-C_3H_7O; 5) C_2H_5, C_2H_5O; 6) C_6H_5, C_6H_5; 7) C_6H_5, C_2H_5O; 8) C_3H_7O, C_3H_7O; 9) C_2H_5O, C_2H_5O; 10) CH_3O, CH_3O.

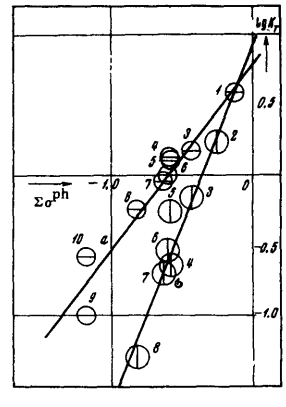


Figure 7. Variation of the tautomeric equilibrium constants ($\lg K_T$) for monothioic phosphorus acids of the type ABPSOH with $\Sigma\sigma^{ph}$ in 7% (*a*) and 80% (*b*) aqueous alcohol (see Table 5, series 13 and 14): 1) C_6H_5O, C_6H_5O; 2) CH_3O, CH_3O; 3) C_2H_5O, C_2H_5O; 4) iso-C_3H_7O, iso-C_3H_7O; 5) ClC_6H_4; ClC_6H_4; 6) iso-C_4H_9O, iso-C_4H_9O; 7) C_3H_7O, C_3H_7O; 8) C_4H_9O, C_4H_9O; 9) CH_3, C_2H_5O; 10) C_6H_5, C_6H_5.

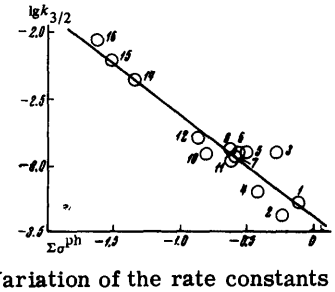


Figure 6. Variation of the rate constants ($\lg k_{3/2}$) for the bromination of derivatives of the type ABP(O)$CH{=}CH_2$ in carbon tetrachloride (see Table 5, series 11): 1) C_6H_5O, C_6H_5O; 2) CH_3O, CH_3O; 3) p-$CH_3C_6H_4O$, p-$CH_3C_6H_4O$; 4) C_2H_5O, C_2H_5O; 5) C_2H_5O, C_3H_7O; 6) iso-C_3H_7O, iso-C_3H_7O; 7) iso-C_4H_9O, iso-C_4H_9O; 8) C_3H_7O, C_3H_7O; 10) C_4H_9O, C_4H_9O; 11) $C_6H_{13}O$, $C_6H_{13}O$; 12) C_6H_5, C_4H_9O; 14) CH_3, C_4H_9O; 15) C_2H_5, C_4H_9O; 16) C_4H_9, C_4H_9O.

4. SEPARATION OF THE CONSTANTS σ^{ph} INTO INDUCTIVE AND RESONANCE COMPONENTS

The application of the constants σ^{ph} to reactions in which the phosphorus atom participates directly and to the physical properties of organophosphorus compounds proved to be more complicated. Numerous examples are known where the correlation with the aid of the constant σ^{ph} does not yield satisfactory results. Thus, in the attempt to correlate the rate constants for the alkaline hydrolysis of compounds of the type ABP(O)X, where X is fluorine or the p-nitrophenyl group (Maklyaev et al.[67]) it was found that the linear relation embraces only groups of similar substances: the data for phosphonates lie on one line and those for phosphates, as it were, lie on another (Fig. 8*a*). Similarly the data of Henderson and Buckler[68] for the rate constants for the alkylation of phosphines with ethyl iodide in acetone

are not correlated with the constants σ^{ph}. The points corresponding to different phosphines in Fig. 9 are distributed in a most peculiar fashion. At the same time the basicities of these phosphines show a satisfactory linear correlation between pK_a (in nitromethane) and $\Sigma\sigma^{ph}$ (Table 4, series 3)[8].

It is noteworthy that in both these and other known cases, where there is no correlation with the σ^{ph}, it is also impossible to achieve a linear correlation with any other known σ constants, for example, σ^* (Fig. 8*b*), σ^0, and others.

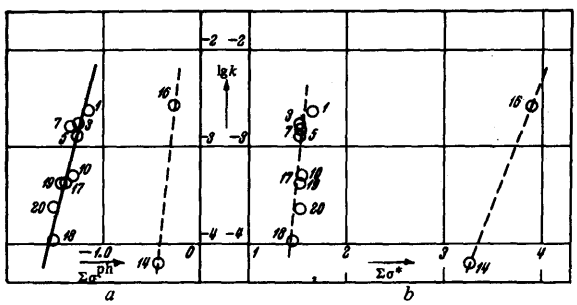


Figure 8. Correlation between the rate constants for alkaline hydrolysis ($\lg k$) of phosphorofluoridates and phosphonofluoridates of the type ABPOF: *a*) with $\Sigma\sigma^{ph}$; *b*) with $\Sigma\sigma^*$: 1) CH_3, C_2H_5O; 3) CH_3, iso-C_3H_7O; 5) CH_3, iso-C_4H_9O; 7) CH_3, iso-$C_5H_{11}O$; 10) C_2H_5, C_2H_5O; 14) C_2H_5O, C_2H_5O; 16) C_2H_5O, C_3H_7O; 17) C_3H_7, C_2H_5O; 18) iso-C_3H_7, C_2H_5O; 19) C_4H_9, C_2H_5O; 20) iso-C_4H_9, C_2H_5O.

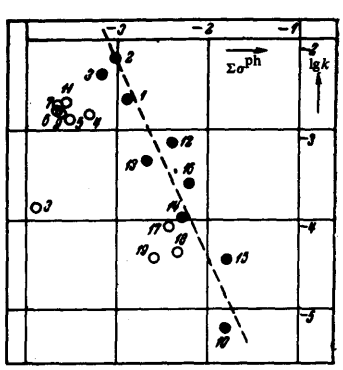


Figure 9. Correlation of the rate constants ($\lg k$) for the alkylation of phosphines of the type R′R″R‴P (according to the data of Henderson and Buckler[68]) with $\Sigma\sigma^{ph}$. The numbers of the points and the substituents R′, R″, and R‴ are indicated: 1) CH_3, CH_3, CH_3; 2) CH_3, CH_3, C_2H_5; 3) CH_3, C_2H_5, C_2H_5; 4) C_2H_5, C_2H_5, C_2H_5; 5) C_3H_7, C_3H_7, C_3H_7; 6) C_4H_9, C_4H_9, C_4H_9; 7) C_4H_9, C_4H_9, C_4H_9 [the second value of $\lg k$ quoted by the authors for $(C_4H_9)_3P$ was employed]; 8) iso-C_4H_9, iso-C_4H_9, iso-C_4H_9; 9) C_5H_{11}, C_5H_{11}, C_5H_{11}; 10) $CNCH_2CH_2$, $CNCH_2CH_2$, $CNCH_2CH_2$; 11) cyclo-C_6H_{11}; cyclo-C_6H_{11}, cyclo-C_6H_{11}; 12) CH_3, CH_3, C_6H_5; 13) C_2H_5, C_2H_5, C_6H_5, 14) C_2H_5, C_6H_5, C_6H_5; 15) C_6H_5, C_6H_5, C_6H_5; 16) *p*-$CH_3OC_6H_4$, *p*-$CH_3OC_6H_4$, *p*-$CH_3OC_6H_4$; 17) C_4H_9, C_4H_9, H; 18) C_8H_{17}, C_8H_{17}, H; 19) iso-C_4H_9, iso-C_4H_9, H.

The complexity of the application of $\sigma\rho$ analysis to organophosphorus reactions of this type and the consequent apparent failure of the universality of the constants σ^{ph} gave rise to a number of papers in which other methods for the correlation analysis of organophosphorus compounds are proposed. These include the correlation of Peppard et al.[24] embracing the carboxylic and phosphonic acid series, the correlation between the NMR chemical shifts of ^{31}P with special constants[69], the constants σ_X^{ph} derived by Knunyants et al.[22] specifically for the hydrolysis of phosphorochloridates, phosphorofluoridates, and *p*-nitrophenyl phosphates, another set of constants for the hydrolysis of the corresponding phosphonates, and a third set for phosphonochlorido-thiolates[26], the correlation of Rozen and coworkers[70] between the extraction constants and the electronegativities of the substituents at the phosphorus atom, the multiparameter correlation of Pal'm et al.[71], etc. All these attempts at correlation in the chemistry of organophosphorus compounds were not developed further, since the constants proposed were not universal and could be applied only to a very limited range of substances and reaction series.

Table 6. Correlation of data[66] for the extraction of actinide salts with the constants σ^{ph} ($\alpha = 1.00$).

No. of series	Extraction	Medium	*n*	$\lg K_e^0$	$\rho+S_\rho$	*r*	*S*
1	$UO_2(NO_3)_2$+R′R″R‴PO[a]	H_2O/C_6H_6	12	−2.16	−1.06	0.973	0.23
2	ditto	$2M$ HNO_3/C_6H_6	15	−0.51	−0.96	0.968	0.22
3	»	$4M$ HNO_3/C_6H_6	13	−0.04	−0.73	0.976	0.16
4	»	$6M$ HNO_3/C_6H_6	15	0.10	−0.61	0.968	0.14
5	»	$8M$ HNO_3/C_6H_6	15	0.10	−0.48	0.907	0.14
6	»	HNO_3/C_6H_6, according to K_e	13	0.12	−0.81	0.975	0.18
7	»[b]	$0.5M$ HNO_3/CCl_4	15	−1.62	−1.32	0.987	0.17
8	»	$1M$ HNO_3/CCl_4	12	−1.11	−1.21	0.981	0.19
9	»	$2M$ HNO_3/CCl_4	14	−0.86	−1.42	0.961	0.21
10	»[c]	H_2O/CCl_4	13	−1.58	−0.80	0.976	0.17
11	»[d]	$0.5M$ HNO_3/C_6H_6	6	−1.89	−1.30	0.986	0.29
12	»[e]	$1M$ HNO_3/CCl_4	8	−0.39	−0.89	0.970	0.26
13	»	$3M$ HNO_3/CCl_4	8	0.74	−0.56	0.924	0.27
14	»	$5M$ HNO_3/CCl_4[f]	8	1.06	−0.41	0.885	0.26
15	»	HNO_3/CCl_4, according to K_e	8	1.00	−0.49	0.932	0.22
16	$Pu(NO_3)_4$+R′R″R‴PO[g]	$0.5M$ HNO_3/CCl_4	14	−1.61	−1.11	0.936	0.32
17	ditto	$1M$ HNO_3/CCl_4	11	−0.89	−0.94	0.921	0.32
18	»	$2M$ HNO_3/CCl_4	14	0.64	−0.27	0.706	0.27
19	»[h]	$2M$ HNO_3/CCl_4	5	−1.24	−1.29	0.966	0.29
20	»	$2M$ HNO_3/CCl_4	5	−1.26	−1.20	0.977	0.26
21	$UO_2(NO_3)_2$+R′R″R‴PO	C_6H_6	10	(log K^e) −2.36	−0.68	0.994	0.26

[a] $c_{UO_2(NO_3)_2} = 0.1$ M; [b] $c_{UO_2(NO_3)_2} = 50$ g litre^{-1}; [c] $c_{UO_2(NO_3)_2} = 0.2$ M; [d] $c_{UO_2(NO_3)_2} = 8.4 \times 10^{-4}$ M; [e] $c_{UO_2(NO_3)_2} = 0.01$ M; [f] On further increase of the concentration of nitric acid, the correlation became greatly impaired; [g] $c_{Pu(NO_3)_4} = 1$ g litre^{-1}; [h] $c_{Pu(NO_3)_4} = 0.9$ g litre^{-1}.

At the same time, the extensive experience gained in the application of the constants σ^{ph} gave rise to the hope that it might be possible to develop correlation methods with the aid of σ^{ph} constants which would be universal and would permit $\sigma\rho$ analysis of the rate and equilibrium constants for a wide variety of organophosphorus compounds in which the phosphorus atom does and does not participate directly.

In order to develop such a system, it was necessary to elucidate first the nature of the electronic effects characterised by the constants σ^{ph}. In the paper quoted above[4], Kabachnik does not deal with the problem of the nature of the constants σ^{ph} at all; this was done for the first time by Pal'm[51], who established two linear relations: between the constants σ^0 of the *meta*-, and *para*-substituents in phenyl groups and the corresponding (for the substituted phenyl groups) constants σ^{ph}:

$$\sigma^{pH} = -0.48 + 0.78\sigma^0 \quad (3)$$

and between the constants σ^{ph} for alkyl substituents and Taft's inductive constants σ^*:

$$\sigma^{ph} = -0.965 + 1.97\sigma^*. \quad (4)$$

Hence Pal'm concluded that the constants σ^{ph} refer to inductive effects. At the same time he took into account the fact that numerous σ^{ph} constants for substituted alkyl, alkoxy-, and many other groups cannot be related by any simple procedure to the known constants σ. He suggested that in the case of such groups one is dealing with a "field effect"—the electrostatic interaction between the charge of the phosphonate or phosphate anion and the dipole of the substituent, which contributes to the constant σ^{ph}. However, this explanation, on which, incidentally, Pal'm does not insist, contradicts many experimental data. Firstly, there are reaction series, readily susceptible to correlation with the constant σ^{ph} in which there are no ionic centres either in the ground or in the transition state. For example, the radical bromination of vinyl derivatives of phosphorus[9], the order of which is 3/2, is a reaction of this type. Secondly, it is difficult to postulate powerful ion–dipole interaction for groups such as phenyl or vinyl, which nevertheless deviate from the linear relation between σ^{ph} and σ^*.

Finally, recently Mastryukova and Kabachnik[52] established that the constants σ^{ph} for aromatic groups are well correlated not only with Taft's σ^0 constants, characterising the inductive effect of the substituents in a phenyl group, but also with the usual σ constants, which include both the inductive and resonance components:

$$\sigma^{ph} = -0.415 + 0.634\sigma. \quad (5)$$

The correlation in the latter case is just as satisfactory. The the concept of the purely inductive nature of the constants σ^{ph} is found not to hold even after corrections for the "field effect".

On the other hand, there are convincing data indicating that the electronic effect of substituents at the phosphorus includes a resonance component. Thus in many studies the concept of d_π–p_π conjugation was invoked by the authors in the discussion of the results of chemical investigations or physical measurements. In their study on the kinetics of the hydrolysis of substituted phosphinyl chlorides, Dostrovsky and Halman[72] attribute the effect of substituents in the phosphinyl group on the rate of hydrolysis to inductive and resonance effects. Other investigators of the kinetics of the substitution reactions (solvolysis, hydrolysis) at a saturated phosphorus atom (Heat[73], Larsson[30], Hudson[74], Maklyaev and coworkers[23,67,75], Bel'skii and coworkers[76,77], etc.) also developed this point of view. In 1962 Kabachnik et al.[6] showed that the constants σ^{ph} of aryl groups can vary under the influence of steric hindrance to conjugation. A systematic description of the evidence in favour of the resonance interaction of the phosphorus atom with the groups joined to it may be found in papers by Hudson[65], Kabachnik[78], Loshadkin[79], etc. At present there is no doubt that the generally adopted hypothesis is valid.

In this connection there arose the idea that the constants σ^{ph} be divided into inductive (σ_I^{ph}) and resonance (σ_R^{ph}) components and that their role in the correlation of the reactivities of organophosphorus compounds be elucidated. Mastryukova[80] reported such subdivision of the constants at the Fourth Conference on the Chemistry and Application of Organophosphorus Compounds at Kazan in January 1969.

In the series of organic phosphorus compounds it was of course impossible to apply the procedures for the subdivision of the constants σ^{ph} into σ_I^{ph} and σ_R^{ph} employed in the aromatic series. In the latter case several methods were used to divide the constants into the inductive and resonance components: the inductive constants were calculated from model reaction series such as ionisation of bicyclo[2,2,2] octane-1-carboxylic acid[81], from Taft's σ^* constants[82], from the ionisation constants of substituted acetic acids[83], or from the ionisation constants of substituted *p*-toluic acids[84] or they were evaluated by comparing the constants σ_p and σ_m put forward by Taft and Lewis[85] and modified by Roberts and Jaffé[86]. With organophosphorus compounds, it was of course impossible to employ any of these methods.

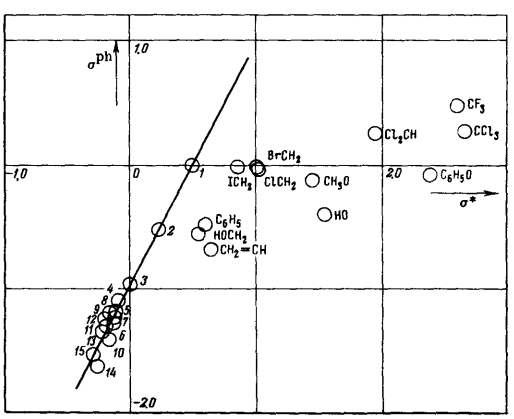


Figure 10. Relation between the constants σ^{ph} and Taft's σ^* constants for the substituents R. The numbers of the points and the substituents R are indicated: 1) H; 2) $C_6H_5CH_2$; 3) CH_3; 4) C_2H_5; 5) C_3H_7; 6) iso-C_4H_9; 7) C_4H_9; 8) cyclo-C_6H_{11}; 9) C_6H_{13}; 10) $(CH_3)_3CCH_2$; 11) iso-C_3H_7; 12) cyclo-C_5H_9; 13) s-C_4H_9; 14) $(CH_3)_3SiCH_2$; 15) $(CH_3)_3C$.

The subdivision of the constants σ^{ph} into σ_I^{ph} and σ_R^{ph} is based on the following considerations. It was noted above that the constants σ^{ph} for alkyl groups are linearly related to Taft's σ^* constants, i.e. they reflect only inductive effects. Fig. 10 shows the correlation between the constants σ^{ph} and σ^* for alkyl groups. Points corresponding to different substituents are also included. They do not lie on the straight line for the alkyl groups but are located to one side, in the direction of higher values of σ^*. It might have been supposed that the inductive effects of all these groups also follow the linear relation shown in Fig. 10 and the

deviations are due to resonance effects. Fig. 11 illustrates this hypothesis: for the points Q we have $OA = \sigma^*$, $AQ = \sigma^{ph}$, $BQ = \sigma_R^{ph}$, and $AB = \sigma_I^{ph}$. It follows from the above that the inductive components of the constants σ^{ph} for these substituents can also be calculated from the constants σ^* using the linear equation†

$$\sigma_I^{ph} = -0.960 + 1.99\,\sigma^* \qquad (6)$$

and the constants σ_R^{ph} can be found by difference

$$\sigma_R^{ph} = \sigma^{ph} - \sigma_I^{ph}.$$

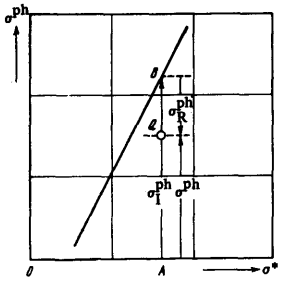


Figure 11. Relation between the constants σ^{ph}, σ_I^{ph}, and σ_R^{ph}.

Thus it has been arbitrarily assumed here that in the ionisation of acids the ratio $\sigma_I^{ph} : \sigma_R^{ph} = 1 : 1$ ($\alpha = 1$, see below).

One must of course bear in mind that the above treatment includes a number of arbitrary assumptions. For example, it is assumed that the inductive effects of alkyl groups follow the same relation as the inductive effects of substituted alkyl, aryl, alkoxy-, and other groups. Analysis of the constants for purely organic reaction series shows that this is not quite true, at least as regards the transmission of inductive effects along a saturated chain[87]. Probably the chemistry of phosphorus provides a better justification for the above hypothesis. This is evident if only from the existence of a unique correlation for all substituted and unsubstituted aromatic and aliphatic phosphorus acids.

The second assumption is that all the deviations from the linear relation (Fig. 10) have been attributed solely to resonance effects, without taking into account steric factors and hyperconjugation. The influence of steric factors on the reactivity of organophosphorus compounds will be discussed below. It is clearly shown only in a few cases. In most of the other cases the large bulk of the phosphorus atom ensures low steric hindrance due to the atoms and groups attached to it. At any rate, steric hindrance is in this case significantly lower than at the carbon atom. The effect of hyperconjugation is also probably slight (see below).

The above assumptions do not of course have a rigorous justification. However, they are no more arbitrary than those made in the separation of the inductive and resonance constants in the aromatic series, which does not preclude their fruitful employment.

† We revised the parameters of the equation, which differ somewhat from those quoted by Pal'm[51].

The constants σ^*, which are necessary in the calculation of inductive constants σ_I^{ph} by Eqn. (6), are presented in column 2 of Table 1. For electronegative substituents such as F, Cl, OH, CF_3, CCl_3, C_6H_5, CH_2=CH, and certain others, the constants σ^* were taken from Pal'm's book[15]; he calculated them from the ionisation constants of substituted acetic acids by the equation

$$\sigma^* = (2.623 - 0.552\,pK_a) \pm 0.034 \qquad (7)$$

using the conversion $\sigma^*_{XCH_2} = 0.388\sigma^*_X$. These constants differ somewhat from those quoted in "The Chemist's Handbook"[88] and are probably more accurate. The constants σ^* for CH_2=$CHCH_2$, $ClCH_2CH_2CH_2$, and other XCH_2 groups were calculated from the corresponding constants for the groups X by multiplying the latter by 0.388.[15]

Table 7. The constants σ^* for RO groups calculated from the ionisation constants of alkoxyacetic acids ($ROCH_2COOH$).[19]

R	pK_a	$\sigma^*_{ROCH_2}$	σ^*_{RO}	σ^*_{RO} calc. from σ_I	
				according to Taft (Ref.29)	according to Charton (Ref.83)
CH_3	3.53	0.67	1.73[a]	1.56; 1.87	—
C_2H_5	3.60	0.64	1.64	1.68	1.68
C_3H_7	3.65	0.61	1.57	1.74	1.68
iso-C_3H_7	3.69	0.59	1.51	—	1.62
C_4H_9	3.66	0.60	1.55	1.93	1.68
iso-C_4H_9	3.67	0.60	1.52	—	—
C_6H_5	3.17	0.87	2.24	—	2.43

[a] $\sigma^* = 1.67 \pm 0.07$ according to Pal'm[15].

Table 8. The constants σ^* for RS groups calculated from the ionisation constants of alkylthioacetic acids ($RSCH_2COOH$).[25,27]

R	pK_a	$\sigma^*_{RSCH_2}$	σ^*_{RS}	σ^*_{RS} calc. from σ_I	
				according to Taft (Ref.29)	according to Charton (Ref.83)
CH_3	3.72	0.57	1.47[a]	1.56	1.56
C_2H_5	3.74	0.56	1.44	1.56	1.56
C_3H_7	3.78	0.54	1.38	1.50	1.50
iso-C_3H_7	3.72	0.57	1.47	1.56	1.56
C_4H_9	3.81	0.52	1.34	1.43	1.43

*$\sigma^* = 1.44 \pm 0.06$ according to Pal'm[15].

The constants σ^* of alkoxy- (RO) and alkylthio- (RS) groups were calculated by the authors of this review. In the first case Palomaa's data[19] were employed. The constants σ^* for $ROCH_2$ groups (Table 7) were evaluated by Eqn. (7) from the ionisation constants of alkoxyacetic acids $ROCH_2COOH$ determined conductimetrically in water at 25 °C and these yielded the corresponding constants for the RO groups on being divided by 0.388. The constants σ^* for $RSCH_2$ groups were evaluated similarly from the data of Ramberg[25] and Larsson[27] from the ionisation constants of alkylthioacetic acids $RSCH_2COOH$ and from them the values for the RS groups were calculated (Table 8). For comparison, Tables 7 and 8 include the values of σ^* for alkoxy- and alkylthio-groups calculated from the constants σ_I by the familiar relation $\sigma^* = 6.23\sigma_I$.

Among aromatic groups, the constants σ* have been reliably determined only for the phenyl group (0.62).[15] In the calculation of the constants σ* for phenyl groups, one resorts sometimes to the relation between σ* and σ^0:

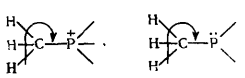
$$\sigma^*_{XC_6H_4} = \sigma^0_X + 0.600. \quad (8)$$

However, the applicability of this relation is very limited[87] and the use of the values of σ* thus obtained in the calculation of σ_I^{ph} gives rise to considerable doubts. Therefore Table 1 lists the constants σ*, σ^{ph}, σ_I^{ph}, and σ_R^{ph} only for the phenyl and pentafluorophenyl groups, the values for the latter having been calculated by an independent method from experimental NMR data[39] for ^{19}F. For the remaining aromatic groups, only the values of σ^{ph} are quoted. The literature sources from which the constants σ* were calculated or taken directly are indicated in column 6 of Table 1.

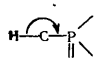
5. INDUCTIVE (σ_I^{ph}) AND RESONANCE (σ_R^{ph}) COMPONENTS OF THE CONSTANTS σ^{ph}

The constants σ_I^{ph} differ of course from the constants σ* by the choice of the starting point of the scale, i.e. the standard substituent: in the σ* scale the standard substituent is the CH_3 group ($\sigma^*_{CH_3} \equiv 0$), while hydrogen is employed as the standard in the σ^{ph} scale ($\sigma_H^{ph} \equiv 0$). Therefore Eqn. (6) contains a constant term of −0.960 equal to the constant σ^{ph} for the methyl group. The coefficient 1.99 in this equation characterises the relation between the σ^{ph} and σ* scales.

As stated in Table 1, the constants σ_R^{ph} for all alkyl groups are equated to zero. Formally this follows from the system employed in the calculation. The physical significance of this corresponds to the assumption that the hyperconjugation effects of the alkyl groups attached to phosphorus are negligible. An attempt to take into account the hyperconjugation effects in the hydrolysis of chlorophosphinates was made by Pal'm et al.[71], but they obtained the hyperconjugation component with the sign reversed, which is contrary to the known S_N2 mechanism of this reaction. Furthermore, the value of h obtained proved to be unusally high and without reasonable physical significance. Theoretically the greatest hyperconjugation effects might be expected in the reactions of organophosphorus compounds where the valence state of phosphorus changes. These include protonation and alkylation of phosphines[8,61,68]. Hyperconjugation, i.e. in this case σd conjugation, should stabilise to a greater extent the phosphonium compound



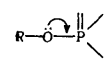
than the phosphine as a result of the contraction of the d orbitals when a positive charge appears[89]. A consequence of this should be an increase of the basicity of phosphines containing methyl groups. However, the basicity of trialkylphosphines decreases in the series $(CH_3)_2PC_2H_5 > (C_2H_5)_2PCH_3 > (CH_3)_3P >$ all remaining phosphines $>$ (iso-C_4H_9)P.[61] In alkylation the same series is maintained. Hence Henderson and Buckler[68] concluded that combined hyperconjugation and steric effects operate. In reactions without change of the valence state of phosphorus, the problem of the possible hyperconjugation



is altogether obscure. In the literature there is no rigorous evidence indicating the existence of this phenomenon. It may be supposed that the hyperconjugation effects in these cases are small if they exist at all.

All the resonance constants of the groups attached to phosphorus are negative. This reflects the fact that phosphorus in its organic compounds behaves as an electron acceptor. For pentavelent (tetracoordinate) phosphorus this has been known for a long time[78,90] and is due both to the presence of an effective positive charge and to vacant low-lying higher atomic orbitals (3d and possibly 4s). It is interesting that in the trivalent state phosphorus also exhibits slight but definite acceptor properties (−M-effect, see Tsvetkov et al.[91] and Schiemenz[92]).

The resonance constants σ_R^{ph} of alkoxy-groups have high absolute magnitudes. This corresponds to a powerful effect of the type



in which the unshared electron pairs of the oxygen atoms partially fill the atomic d orbitals of phosphorus forming molecular d_π–p_π orbitals‡.

With increase in the size of the alkoxy-group σ_R^{ph} decreases. The constants σ^{ph} for alkoxy-groups, which have small absolute magnitudes, consist of the sum of a large negative σ_R^{ph} and a somewhat smaller but still large positive σ_I^{ph}. Thus alkoxy-groups attached to phosphorus have large resonance and inductive effects acting in opposition. This is particularly characteristic of the phenoxy-group for which σ^{ph} is close to zero (−0.06), while $\sigma_R^{ph} = -2.89$ and $\sigma_I^{ph} = 2.83$.

The resonance constants of alkylthio-groups differ from those of alkoxy-groups by having smaller absolute magnitudes. In this case the relative influence of the inductive effects is greater and for the C_2H_5S group σ^{ph} is positive. Probably this is due to the smaller p-component of the atomic orbitals of sulphur compared with oxygen[93], as a result of which purely resonance interaction is weaker.

The inductive and resonance components of the constants σ^{ph} of halogens (fluorine and chlorine) attached to phosphorus have the greatest absolute magnitudes: $\sigma_I^{ph} = 5.21$ and $\sigma_R^{ph} = -4.65$ for fluorine and $\sigma_I^{ph} = 4.37$ and $\sigma_R^{ph} = -3.44$ for chlorine. This is evidence of intense electron withdrawal by an inductive effect and a somewhat weaker mesomeric effect. As a result σ^{ph} are large and positive.

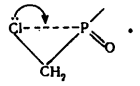
In general, it should be noted that there is a definite parallelism between the absolute values of σ_R^{ph} and σ_I^{ph} for the groups examined above: the greater the degree of withdrawal of electrons by the inductive effect the greater is the injection of electrons by the resonance effect. Possibly this is a consequence of the increase of the effective

‡ In all cases we are considering the participation of the atomic d orbitals of phosphorus following the concept generally adopted in the literature. The participation of atomic 4s or hybrid orbitals is disregarded. This problem is still not quite clear and requires special investigation.

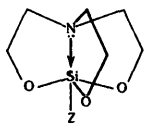
positive charge of the phosphorus by the inductive withdrawal of electrons. The atomic *d* orbitals of phosphorus then contract, which in turn leads to improved conditions for $d-p$ overlapping[89]. The parallel variation of the constants σ_I and σ_R has also been noted in the literature[94], particularly in those cases where the substituents compared have the same first atom, attached to the transmitting system. Then, for rigorously similar substituents, there is a linear relation between σ_R and σ_I.[95]

The resonance constants of the phenyl and vinyl groups have much smaller absolute values than those for alkoxy-groups. The π-electron system of the benzene ring or the double bond gives up its electrons to the *d* orbitals of phosphorus to only a slight degree. This is well known in view of the weak conjugation effects characteristic of aromatic and vinyl phosphorus compounds[78].

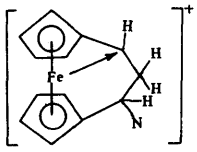
The fairly high values of σ_R^{ph} for groups such as $ClCH_2$, $BrCH_2$, Cl_2CH, and Cl_3C is striking. In the chemistry of aromatic compounds these groups are characterised by almost pure inductive effects. It may be supposed that resonance effects are in this case associated with the direct overlapping of the orbitals of the unshared electron pairs of chlorine with the *d* orbitals of phosphorus, forming a dative bond, which can be conventionally represented thus:



This effect is most characteristic of α-substituted derivatives; it is weaker for β-halogeno-derivatives and is virtually absent for γ-halogeno-derivatives. It is specific to phosphorus and probably to other elements with vacant *d* orbitals. Thus $p-d$ bonds of this type in organosilicon compounds have been discussed in the literature. As an example, one may quote the transannular $p-d$ bond in silatranes (triptychsiloxazolidines), first suggested by Frye et al.[96]:



It is interesting that a direct intramolecular donor-acceptor bond in ferrocene has been discussed by Richards and Hill[97] in connection with the stability of carbonium ions, for example:



This type of bond with phosphorus is probably present also in other groups with atoms having unshared electron pairs or π bonds in the α- or β-positions, formally separated from the phosphorus atoms by CH_2 groups. These include groups such as $CH_2OH(\sigma_R^{ph} = -0.69)$, $C_6H_5OCH_2$ $(\sigma_R^{ph} = -0.9)$, $C_2H_5OCH_2CH_2$ $(\sigma_R^{ph} = -0.35)$, $N{\equiv}CCH_2CH_2$ $(\sigma_R^{ph} = -1.22)$, $CH_2{=}CHCH_2$ $(\sigma_R^{ph} = -0.33)$, and even $C_6H_5CH_2$ $(\sigma_R^{ph} = -0.16)$.

6. CORRELATION BETWEEN THE RATE CONSTANTS FOR NUCLEOPHILIC SUBSTITUTION AT THE PHOSPHORUS ATOM

There is every reason to suppose that in nucleophilic substitution reactions at the phosphorus atom the relative contributions of the inductive and resonance components are different than in the ionisation of phosphorus acids. It has now been established that in the nucleophilic attack on phosphorus acid esters or esterified acid halides and similar compounds the transition state has the configuration of a trigonal bipyramid, and there is reason to believe that the *d* orbitals of phosphorus participate in its formation. If this model is correct, then substituents capable of $p-d$ conjugation (with a $+M$-effect) should sharply reduce the rate of nucleophilic substitution. In the estimation of their influence in $\sigma\rho$ analysis this should affect the contribution of the resonance σ_R^{ph} constant, namely it should increase it. Therefore it was to be expected that in the correlation of solvolysis and other nucleophilic substitution reactions the equation

$$\lg \frac{k}{k^0} = \rho\Sigma(\sigma_I^{ph} + \alpha\sigma_R^{ph}) \qquad (9)$$

would hold for $\alpha > 1$.

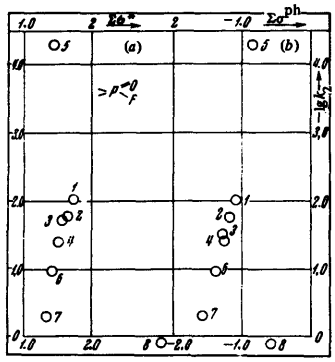


Figure 12. Correlation of the rate constants ($\lg k$) for the alkaline hydrolysis of the fluorides of phosphorus acids of the type ABPOF according to Larsson's data[30]: *a*) with Taft's σ^* constants; *b*) with the constants σ^{ph}. The substituents A and B for the acid fluorides are indicated: 1) CH_3, CH_3O; 2) CH_3, C_2H_5O; 3) CH_3, C_3H_7O; 4) CH_3, iso-C_3H_7O; 5) CH_3, C_2H_5S; 6) C_2H_5, iso-C_3H_7; 7) iso-C_3H_7, iso-C_3H_7O; 8) iso-C_3H_7O, iso-C_3H_7O.

Fig. 12 shows the correlation between the rate constants for the alkaline hydrolysis of phosphorus acid fluorides of the type APBOF on the basis of Larsson's experimental data[30]: two of the graphs (*a* and *b*) show the variation of $\lg k$ with $\Sigma\sigma^*$ and $\Sigma\sigma^{ph}$. Evidently there is no general correlation here, in agreement with previous findings. Fig. 13 shows the correlation between $\lg k$ and $\Sigma(\sigma_I^{ph} + 1.5\sigma_R^{ph})$. Here the points corresponding to di-isopropyl phosphorofluoridate (*8*), bis-(*NN*-dimethyl)phosphorodiamidic fluoride (*9*), (*NN*-dimethyl)methylphosphonamidic fluoride (*10*), and ethyl methylphosphonofluoridothiolate (*5*) together with

all the points for alkyl methylphosphonofluoridates fit very closely the linear relation. This means that in the $\sigma\rho$ analysis of the hydrolysis reactions of acid fluorides the resonance effects make a contribution 1.5 times as great ($\alpha = 1.5$) as in the ionisation of acids. The above corelation ($r = 0.95$, $S = 0.23$, $S_\rho = 0.13$) is remarkable, because here the rate constants vary by 8 powers of 10 ($\lg k$ varies from −4.26 to 4.29).

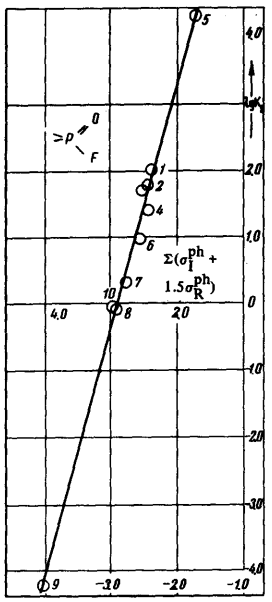


Figure 13. Variation of the rate constants ($\lg k$) for the alkaline hydrolysis of the fluorides of phosphorus acids of the type ABPOF according to Larsson's data [30] with $\Sigma(\sigma_I^{ph} + 1.5\sigma_R^{ph})$. For substances *1–8*, see Fig. 12; 9) $(CH_3)_2N$, $(CH_3)_2N$; 10) CH_3, $(CH_3)_2N$.

The coefficient $\alpha = 1.5$ is an optimum in this case, since poorer correlations are obtained with smaller and greater values of α. For all the reaction series discussed below, optimum values of α are also quoted.

Table 9 presents the results of the correlations between the rate constants for the solvolysis of compounds of the type ABP(O)X, where X = F, p-$NO_2C_6H_4O$, or Cl at different temperatures and in different media. In the hydrolysis of the acid fluorides and p-nitrophenyl esters the coefficient α varies in the range 1.5–1.55 (Table 9, series 1–8). In the solvolysis of acid chlorides in ethanol α = 1.30 (Table 9, series 13 and 14); for the hydrolysis of the chlorides in aqueous acetone, two values are quoted in Table 9—$\alpha = 1.5$ calculated from the experimental data of Hudson and Keay [74] (series 9) and $\alpha = 1.85$ calculated from the data of Neimysheva et al. [100] (series 10). The reason for this discrepancy is obscure. At any rate, it is evident that α depends not only on the type of reaction but probably also on the temperature and the medium.

Resonance effects play a major role in the hydrolysis of the chlorides of thionic acids of phosphorus (series 15 and 16); here $\alpha = 1.8$. The high contribution of the resonance component is in this case probably related to the high effective positive charge of the phosphorus atom [89], which leads to intensified d_π–p_π conjugation.

All the reaction series quoted in Table 9 are characterised by high positive values of the constants ρ, which is probably due to the high polarity of the transition states. Positive values of ρ correspond to an S_N2 mechanism. Substituents which increase the electron density at the phosphorus atom, i.e. with large negative values of $\Sigma(\sigma_I^{ph} + \alpha\sigma_R^{ph})$ retard the reaction and conversely.

Table 10 presents data for the hydrolysis of the alkyl esters of phosphorus acids. Alkaline hydrolysis of ethylphosphonates at 59.2 °C is characterised by $\alpha = 1.6$ according to the data of Hudson et al. [99] (series 1), while according to the data of Bel'skii and coworkers [76,77] (series 3) the alkaline hydrolysis of ethylphosphinates at 80 °C is characterised by a lower value: $\alpha = 1.25$. Possibly this discrepancy is due to a difference in the experimental conditions. Both series have high values of ρ, which corresponds to nucleophilic attack by the hydroxide ion.

Table 9. Correlation of the rate constants for the solvolysis of compounds of the type ABP(Z)X with the constants σ_I^{ph} and σ_R^{ph}.

No. of series	Reaction	Temp., °C	Medium	n	α	$\lg k^0$	$\rho \pm S_\rho$	r	S	Refs
1	ABPOF+OH^-	25	H_2O	10	1.50	10.85	3.75±0.13	0.995	0.23	30
2	ABPOF+OH^-	25	H_2O	17[a]	1.55	6.09	1.72±0.18	0.923	0.30	22, 23
3	ABPO($OC_6H_4NO_2$-*p*)+OH^-	37.5	H_2O	12	1.50	4.34	2.90±0.19	0.979	0.21	12
4	ABPO($OC_6H_4NO_2$-*p*)+OH^-	25	H_2O	6	1.50	7.29	3.14±0.26	0.987	0.14	23
5	ABPO($OC_6H_4NO_2$-*p*)+OH^-	20	H_2O	7	1.50	8.08	3.51±0.61	0.932	0.24	22
6	ABPO($OC_6H_4NO_2$-*p*)+OH^-	25	H_2O	8	1.50	7.50	3.22±0.36	0.965	0.17	22
7	ABPO($OC_6H_4NO_2$-*p*)+OH^-	35	H_2O	8	1.50	7.45	3.11±0.36	0.962	0.17	22
8	ABPO($OC_6H_4NO_2$-*p*)+OH^-	45	H_2O	8	1.50	7.22	2.93±0.34	0.962	0.16	22
9	ABPOCl+H_2O	0	95% $(CH_3)_2CO$	11	1.50	10.22	4.64±0.74	0.901	0.35	74
10	ABPOCl+H_2O	0	95% $(CH_3)_2CO$	5	1.85	11.12	5.05±0.84	0.961	0.20	100
11	ABPOCl+H_2O	0	95% $(CH_3)_2CO$	9	(1.00)[b]	9.48	5.98±0.86	0.928	0.53	71
12	ABPOCl+H_2O	−40	95% $(CH_3)_2CO$	9	(1.00)[b]	12.65	7.05±1.18	0.914	0.51	71
13	ABPOCl+C_2H_5OH	25,2	C_2H_5OH	5	1.30	7.00	5.64±0.45	0.991	0.04	72
14	ABPOCl+C_2H_5OH	39,6	C_2H_5OH	5	1.30	6.86	5.34±0.68	0.976	0.19	72
15	ABPSCl+H_2O	0	95% $(CH_3)_2CO$	6	1.80	9.44	5.61±0.76	0.965	0.21	100
16	ABPSCl+H_2O	30	95% $(CH_3)_2CO$	6	1.80	13.73	7.26±0.77	0.978	0.21	100

[a] The point corresponding to di-isopropyl phosphorofluoridate was excluded.
[b] The coefficient α is unknown since the substituents varied exhibit only an inductive effect.
*Studies the data from which were used for the correlations.

On the other hand, neutral hydrolysis of alkylphosphinates (Table 10, series 4) has a low value of ρ (0.93), which is evidence of low polarity at the transition state. Here the rate of reaction is very low ($\lg k^0 = -5.27$) and $\alpha = 0.90$. Efremov et al.[101] recently established that in this case there is attack on the carbon of the alkyl group with subsequent dissociation of the alkyl–oxygen bond. Here too the S_N2 mechanism is reflected in a positive value of ρ.

Table 10. Correlation of the rate constants for the hydrolysis of phosphorus acid esters in an aqueous medium with the constants σ_I^{ph} and σ_R^{ph} [$\lg k = \lg k^0 + \rho\Sigma(\sigma_I^{ph} + \alpha\sigma_R^{ph})$].

No. of series	Reaction	Temp., °C	n	α	$\lg k^0$	$\rho \pm S_\rho$	r	S	Refs.*
1	RPO $(OC_2H_5)_2$+OH^-	59.2	5	1.60	5.40	4.50±0.39	0.989	0.14	99,110
2	RPO(iso-$C_3H_7O)_2$+OH^-		5	(1.00)[a]	4.12	4.40±0.31	0.992	0.14	99,110
3	RR'PO (OC_2H_5)+OH^-	80	17	1.25	2.72	2.58±0.28	0.920	0.56	76,77
4	RR'PO (OC_2H_5)+H_2O	90	17	0.90	−5.27	0.93±0.06	0.971	0.18	76,77

[a] The coefficient α is unknown since the substituents varied only the inductive effect.
*Studies the data from which were used for the correlations.

An interesting reaction series, investigated by Neimysheva et al.[26], consists in the hydrolysis of alkyl phosphonochloridothiolates R(RS)POCl in 95% aqueous acetone and 0°C. The correlation data ($n = 11$, $\alpha = 1.65$, $\lg k^0 = 3.08$, $\rho = 1.82 \pm 0.27$, $r = 0.914$, and $S = 0.14$) indicate a profound difference between the hydrolysis of these compounds and that of other substances of the type ABPOCl.

Here ρ is unusually low for the hydrolysis of acid chlorides. It would probably be of interest to investigate this reaction in greater detail. There is no doubt that steric effects play a major role in it, as is in fact pointed out by the authors. Therefore the points corresponding to phosphonothiolates with isopropyl and s-butyl groups at the phosphorus atom were excluded in the calculation of the correlation parameters.

7. CORRELATION BETWEEN PHYSICOCHEMICAL DATA

Considerable interest attaches to the correlation between the equilibrium constants for the formation of complexes of various phosphoryl compounds with alcohols and phenols. The complexes are formed as a result of hydrogen bonding:

$$\rangle C{-}OH \ldots O{=}P\langle$$

These reactions were investigated by infrared spectroscopy mainly by Gramstad and coworkers[102-104].

On complete transfer of a proton, i.e. when an acid–base reaction takes place, the coefficient α is unity (Tables 2–4). It is reasonable to suppose that inductive effects play a major role in the formation of a hydrogen bond and therefore one may expect that the coefficient α will be less than unity. Indeed in all cases quoted in Table 11 α varies from 0.80 to 1.00. The lower is the acidity of the proton donor the smaller is α. Thus $\alpha = 0.80$ for the methanol complex, $\alpha = 0.90$ for the phenol and β-naphthol complexes, $\alpha = 0.95$ for the pentachlorophenol complex, and finally $\alpha = 1.00$ in the formation of a hydrogen bond with hydroxyphosphonium ions:

$$R_3P{=}O \ldots HO{-}\overset{+}{P}R_3.$$

All these reaction series are characterised by low negative values of ρ. A negative value of ρ shows that the equilibrium constant increases with increasing electron density at the phosphoryl oxygen atom. Electron-donor substituents of course increase the stability of the hydrogen bond. These effects are naturally small, in agreement with the low values of ρ.

Interesting complexes with iodine have been investigated by a similar method (series 10 and 11). Here the association constants are low ($\lg K^0 = 0.24$ at 20°C), but ρ is negative in this case too and consequently the iodine molecule adds as an electrophilic agent.

Table 11. Correlation of the association constants ($\lg K_{ass}$) in carbon tetrachloride determined from infrared spectra with the constants σ_I^{ph} and σ_R^{ph} [$\lg K_{ass} = \lg K_{ass}^0 + \rho\Sigma(\sigma_I^{ph} + \alpha\sigma_R^{ph})$].

No. of series	Reaction	Temp., °C	n	α	$\lg K_{ass}^0$	$\rho \pm S_\rho$	r	S	Refs.*
	Formation of Hydrogen Bonds								
1	$CH_3OH \ldots O{=}P\langle$	20	13	0.80[a]	1.17	−0.16±0.01	0.968	0.06	102
2	$CH_3OH \ldots O{=}P\langle$	50	13	0.80[a]	0.87	−0.11±0.01	0.963	0.05	102
3	$C_6H_5OH \ldots O{=}P\langle$	20	13	0.90	2.32	−0.34±0.03	0.962	0.13	102
4	$C_6H_5OH \ldots O{=}P\langle$	50	13	0.90	1.95	−0.30±0.02	0.976	0.09	102
5	α-$C_{10}H_7OH \ldots O{=}P\langle$	20	14	0.90	2.36	−0.37±0.02	0.978	0.10	102
6	α-$C_{10}H_7OH \ldots O{=}P\langle$	50	14	0.90	1.96	−0.34±0.02	0.980	0.09	102
7	$C_6Cl_5OH \ldots O{=}P\langle$	20	14	0.95[b]	1.87	−0.44±0.03	0.973	0.12	102
8	$C_6Cl_5OH \ldots O{=}P\langle$	50	14	0.95[b]	1.54	−0.41±0.01	0.973	0.11	102
9	$\rangle\overset{+}{P}{-}OH \ldots O{=}P\langle$	C	7	1.00	2.34	−0.67±0.08	0.968	0.09	35
	Formation of Iodine Complexes								
10	$I_2 \cdot O{=}P\langle$	20	6	1.00[d]	0.24	−0.54±0.06	0.973	0.17	104
11	$I_2 \cdot O{=}P\langle$	50	6	0.95[d]	0.23	−0.44±0.04	0.984	0.12	104

[a] The authors correlate $\lg K_{ass}$ with $\Sigma\sigma^*$,[102] but in this case the correlation is much worse; at 20°C $r = 0.934$, $S = 0.09$, and $S_\rho = 0.01$ and at 50°C $r = 0.919$, $S = 0.08$, and $S_\rho = 0.01$.
[b] In the correlation of $\lg K_{ass}$ with $\Sigma\sigma^*$ at 20°C $r = 0.935$, $S = 0.19$, and $S_\rho = 0.03$ and at 50°C $r = 0.934$, $S = 0.17$, and $S_\rho = 0.03$.
[c] In nitromethane at room temperature.
[d] In the correlation of $\lg K_{ass}$ with $\Sigma\sigma^*$ at 20°C $r = 0.926$, $S = 0.28$, and $S_\rho = 0.06$ and at 50°C $r = 0.929$, $S = 0.25$, and $S_\rho = 0.05$.
*Studies the data of which were used for the correlations.

Gramstad and coworkers[102-104] correlated the association constants for the complexes of organophosphorus compounds with alcohols, phenols, and iodine with Taft's σ^* constants. Linear relations were observed, but the correlation coefficients were much lower than those in Table 11 (see the footnote to this Table).

Table 12. Correlation of half-wave potentials $E_{1/2}$ for the polarographic reduction of organophosphorus aldehydes and ketones with the constants σ_I^{ph} and σ_R^{ph} [$E_{1/2} = E^0_{1/2} + \rho\Sigma(\sigma_I^{ph} + \alpha\sigma_R^{ph})$].

No. of series	Reaction	Temp., °C	Medium	n	α	$E^0_{1/2}$	$\rho \pm S_\rho$	r	S	Refs.*
1	R'R"P(O)CH_2CHO+e	20	H_2O	4	1.40	−0.90	0.28±0.03	0.987	0.01	105
2	R'(RO)P(O)$COCH_3$+e	20	DMF	8	1.40	−1.14	0.06±0.03	0.991[a]	0.03	106
3	R'(RO)P(O)COC_6H_5+e	20	DMF	12	1.25	−0.72	0.08±0.02	0.991[a]	0.02	107

[a] The correlation coefficient was calculated after rotating the coordinate axes by 45°.
*Studies the data from which were used for the correlations.

Razumov, Savicheva, and coworkers[105-107] investigated the polarographic reduction of organophosphorus oxo-compounds and observed a slight but nevertheless definite dependence of the half-wave potentials on the substituents at the phosphorus atom. Table 12 shows the correlation between the experimental data and the constants σ_I^{ph} and σ_R^{ph}. The positive values of the constant ρ indicate, as stated by the authors, that the potential-determining stage of the process consists in the addition of an electron to the molecule of the phosphorylated oxo-compound. Unexpectedly α proved to be greater than unity in these reactions, which undoubtedly indicates the participation of the phosphoryl group in the reduction process.

Table 13 lists data on the correlation between the chemical shifts in the ^{19}F NMR spectra of fluorine-containing organophosphorus compounds. In all cases α is close to unity and high correlation coefficients are obtained regardless of the type of compound.

There are literature data[111-113] for the ^{19}F NMR shifts in the spectra of phosphorus acid chlorides of the type ABPOF, i.e. compounds in which fluorine is linked directly to phosphorus. The attempts to correlate the chemical shifts in the ^{19}F NMR spectra of these compounds with the constants σ_I^{ph} and σ_R^{ph} and also with any other known σ constant were not successful.

A correlation between the ^{35}Cl NMR frequencies for compounds of the type $APOCl_2$ with the constants σ^{ph} was published by Tsvetkov et al.[114] Two linear relations were observed: one for the dichlorides of unsubstituted alkylphosphonic acids and another for the dichlorides of alkylphosphoric, vinylphosphonic, and arylphosphonic acids. When the constants σ_I^{ph} and σ_R^{ph} are used and the available data[114-116] for all substances of the type ABPOCl (where A and B can also be chlorine or fluorine atoms) are treated, then, with the exception of POF_2Cl, all the remaining data are satisfactorily correlated with $\Sigma(\sigma_I^{ph} + 1.20\sigma_R^{ph})$ (r = 0.970) (Table 13, series 10).

8. SPECIFICITY OF THE CONSTANTS σ^{ph}. STERIC EFFECTS

There is of course the problem of the relation between the constants σ^{ph}, σ_I^{ph}, and σ_R^{ph} on the one hand and the constants characterising the polar effects of substituents in the chemistry of carbon compounds: σ^*, σ_p, σ_m, σ^0, etc. Above it was noted that the inductive constants of the substituents σ_I^{ph} attached to phosphorus atoms differ from Taft's inductive constants σ^* only by the scale and the starting point adopted for their calculation. Thus the constants σ_I^{ph} can be derived from the constants σ^*. The constants σ^{ph} for aromatic groups can also be derived from the σ or σ^0 for the corresponding constituents in the aromatic ring[51,52]. Probably these two relations are the only ones between the constants σ^{ph} and other σ constants derived for purely organic compounds. The constants σ^{ph}

Table 13. Correlation of the ^{19}F and ^{35}Cl NMR data for organophosphorus compounds with the constants σ_I^{ph} and σ_R^{ph}.

No. of series	Compound	Medium	n	α	δ_0	$\rho \pm S_\rho$	r	S	Refs.*
	^{19}F-NMR								
1	$X_3PC_6H_4F$ δ_m	CCl_4, CCl_3F	7	0.85	−1.71	−0.97±0.15	0.947	0.52	108
2	$X_3PC_6H_4F$ δ_p	CCl_4, CCl_3F	8	1.10	−1.33	−2.21±0.21	0.974	1.10	108
3	$X_2PC_6F_5$ δ_m	CCl_3F	9[a]	0.85	−0.18	−0.69±0.04	0.990	0.21	39
4	$X_2PC_6F_5$ δ_p	CCl_3F	10	1.00	−4.23	−2.32±0.20	0.972	0.86	39
5	$X_3PC_6F_5$ δ_m	CCl_3F	12	0.80	0.02	−0.60±0.04	0.980	0.24	109
6	$X_3PC_6F_5$ δ_p	CCl_3F	12	0.90	−2.89	−1.84±0.15	0.967	0.83	109
7	$X_3P(O)C_6F_5$ Φ_m^b	CCl_3F	4	1.00	158.7[c]	−1.06±0.14	0.984	0.23	109
8	$X_3P(O)C_6F_5$ Φ_p^b	CCl_3F	4	0.90	147.2[c]	−3.36±0.11	0.999	0.18	109
9	XYZP=NC_6H_4F δ_p	CCl_4	12	1.00	13.50	0.90±0.06	0.982	0.20	31
10	^{35}Cl-NMR ABPOCl	—	28	1.20	27.89[d]	1.91±0.09	0.970	0.45	111, 115, 116

[a] The point corresponding to the PF_2 group was excluded (see Ref. 39).
[b] C_6F_5; Φ = 163.0 p.p.m.
[c] The values of Φ^0.
[d] The value of ν^0.
*Studies (with the exception of Ref. 31) the data from which were used for the correlations.

are compared in Fig. 14 with the constants σ_p for substituents in the aromatic ring. On the basis of this figure, it is difficult to arrive at any conclusion more definite than the statement that the constants agree as regards sign. Since the inductive components of the constants are linearly related, one may conclude that the reason for the differences lies in the resonance components.

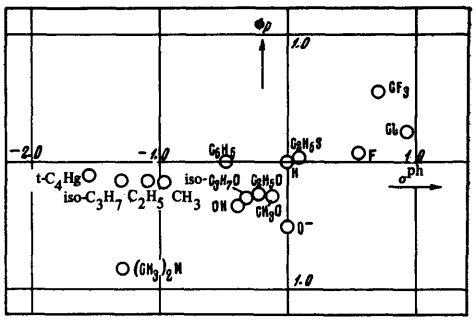


Figure 14. Relation between the constants σ^{ph} and σ_p for different substituents.

The resonance components of the constants σ^{ph} and σ_p, i.e. σ_R^{ph} and σ_R, are compared in Fig. 15. Evidently there is no simple relation between them. This is also found when the constants σ_R^0 are employed. Probably there are fundamental differences between the resonance effects in p_π–p_π conjugated systems and the conjugation effects in systems with a central phosphorus atom (d_π–p_π conjugation), associated with differences between the symmetries and other properties of atomic p and d orbitals. Thus σ^{ph} are specific constants.

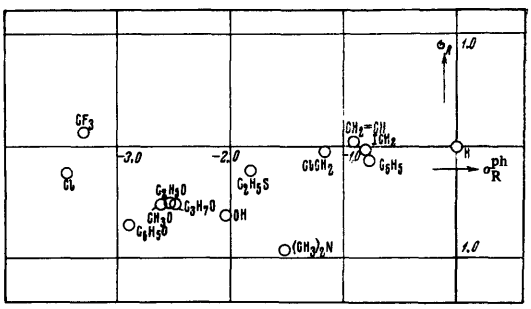


Figure 15. Relation between the constants σ_R^{ph} and σ_R for different substituents.

Rakshys et al.[108] successfully correlated the inductive and resonance constants σ_I and σ_R^0 for groups attached to trivalent phosphorus in phosphorylated fluorobenzene derivatives ($R_2PC_6H_4F$) and chemical shifts in the ^{19}F NMR spectra of these compounds. However, the principles of this correlation could not be extended to compounds of pentavalent (tetracoordinate) phosphorus.

We must now consider the effect of steric factors. This problem has been frequently discussed in the literature. The most pronounced effect of steric factors is observed in the alkylation of tertiary phosphines with alkyl halides. Henderson and Buckler[68] investigated the kinetics of the addition of ethyl iodide to tertiary aliphatic and aromatic phosphines. Although they did see a very limited dependence of the rate constants on the constants σ^*, only a few points in their graph fit a linear relation. The authors ascribe all the deviations to steric and hyperconjugation effects. In the correlation of the rate constants for the hydrolysis of dialkylphosphinic chloride in a neutral medium, Pal'm et al.[71] included Taft's E_S constants characterising steric effects and also the corresponding cross terms. Some workers, who have investigated the correlation of equilibrium or rate constants for reactions of organophosphorus compounds with the constants σ^*, σ^0, and σ_p and who observed deviations from linearity, attributed the latter to the effect of steric factors. Since in many cases these deviations are not observed when the constants σ^{ph} (or $\sigma_I^{ph} + \alpha\sigma_R^{ph}$) are employed, the conclusion that steric factors are responsible for these deviations must be treated with caution.

In general it may be supposed that, in reactions of organophosphorus compounds with participation of the phosphorus atom, steric effects play a smaller role than in the corresponding reactions of purely carbon compounds. This is related to the important fact that the phosphorus atom has a much greater radius than the carbon atom. Therefore for the tetrahedral structures of the initial or final compound and the trigonal bipyramid structure of the transition state, the difference between the hindering groups at the phosphorus atom is greater than at the carbon atom which means that the steric hindrance to the approach of the attacking agent is smaller.

It may be supposed that in all the correlations presented in Tables 2–6 the effect of steric factors is negligibly small. Nevertheless it must be noted that in the alkaline hydrolysis of *p*-nitrophenyl esters of phosphorus acids, investigated by Fukuto et al.[12,98], the point corresponding to compound with a t-butyl group at the phosphorus atom deviates from the linear relation (this point was disregarded in the correlation; Table 9, series 3). There is no doubt that the steric hindrance due to the bulky t-butyl group has an effect here. There is also no doubt that in the hydrolysis of phosphinic chlorides and even phosphonochloridates, investigated by Neimysheva et al.[71], the steric hindrance due to the isopropyl and isobutyl groups reduces the rate constant for S_N2 attack.

In Fig. 9 discussed above the filled circles correspond to tertiary phosphines containing only small alkyl groups or phenyl rings. These points are concentrated near the straight line drawn in the diagram. For these phosphines, the steric hindrance is least and there is a tendency towards a linear relation. All the substances containing higher alkyls (starting with propyl) markedly deviate towards lower rate constants. The deviations are particularly pronounced for tri-isobutylphosphine, the steric hindrance for which should be a maximum. At the same time, in the protonation of the same phosphines (Fig. 4 and Table 4, series 3), steric hindrance may in fact have an effect on the positions of the points near the straight line, but in this case the deviations are small and quite satisfactory correlation is observed ($r = 0.950$). In reactions of nitrogen compounds the greatest steric hindrance is observed in the alkylation of tertiary amines (the Menshutkin reaction) and in the formation of complexes with trimethyl-

boron[117]. In reactions of organophosphorus compounds steric hindrance is much less and yet it does have an effect in the alkylation of tertiary phosphines and in certain solvolysis reactions.

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All the correlations quoted above were calculated by least squares using Jaffé's method[2]. Tables 2–6 and 9–13 show that 124 reaction series were employed—for the equilibria and reactions of organophosphorus compounds.

Table 14.

Quality of correlation	r	Percentage of total number	
		This review	Jaffé's review (Ref.2)
Very good	>0.989	25	32.4
Good	0.970—0.989	37	24
Quite Satisfactory	0.950—0.970	20	13.7
Satisfactory	0.900—0.950	14	9.9
Poor	<0.900	4	20

These series include about 1300 individual constants. The statistical distribution of the correlation coefficients is shown in Table 14, according to which the number of very good and satisfactory correlations for organophosphorus compounds is somewhat greater (62%) than in Jaffé's compilation (56.4%), but the number of very good correlations is somewhat less and that of poor correlations is significantly less. It should be borne in mind that in many cases considerable experimental difficulties arise in the measurement of the rate constants for reactions of organophosphorus compounds and reduce the accuracy so that some of the σ^{ph} constants employed require revision. These revisions may alter the parameters of the individual correlations. However, there is no doubt about the wide applicability of correlation analysis to a wide variety of reactions and equilibria of organophosphorus compounds when the constants σ^{ph} or σ_I^{ph} and σ_R^{ph} (of different relative values) are employed.

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Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow

U.D.C. 547.31

Ionic Hydrogenation

D.N.Kursanov and Z.N.Parnes

Papers on the ionic hydrogenation of a double bond, consisting in the successive addition of a proton and a hydride ion, are surveyed. The use of trifluoroacetic acid as donor of the proton and of triethylsilane as donor of the hydride ion has permitted the hydrogenation of alkenes, dienes, cyclopropane hydrocarbons, saturated and unsaturated ketones, aldehydes, quinones, and anils. Each class of compounds shows selectivity on ionic hydrogenation with the above pair of hydrogenating agents. The reaction extends to single bonds in the case of disulphides and ethers, which undergo ionic hydrogenolysis. Ideas on the mechanism of ionic hydrogenation are examined.

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I. INTRODUCTION

Interest in the hydrogenation of unsaturated organic compounds arose in an early stage of the development of organic chemistry. The outstanding event in this field was the discovery of hydrogenation on heterogeneous catalysts. This discovery led to the founding of new branches of organic and physical chemistry, and also acquired important industrial applications.

Intense study of hydrogenation reactions continues at the present time, the reason being the great practical and theoretical interest of hydrogenation. Each of the proposed methods of hydrogenation has fundamental limitations as well as its own merits. In particular, such methods frequently do not possess the required selectivity.

Reactions involving hydrogenation in the presence of complex organometallic catalysts under homogeneous conditions are being comprehensively investigated at the present time. Complex metal hydrides are being widely used in practical hydrogenation.

A special place among methods of hydrogenation is occupied by reactions involving stages of successive addition of a proton and of a hydride ion to the substance to be hydrogenated:

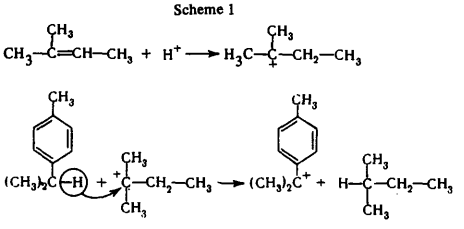
$$A{=}E + H^+ \rightleftarrows AH{-}E^+ \xrightarrow{+H^-} AH{-}EH\ .$$

The above is not the only possible path of ionic hydrogenation. A different sequence of stages can be imagined, the first stage being addition of the hydride ion, and addition of a proton to the resulting carbanion the second stage. Ionic hydrogenation reactions are also possible involving the transfer of two electrons and two protons. However, the present Review will be confined to reactions of ionic hydrogenation taking place solely by the first route, which for brevity we shall term reactions of ionic hydrogenation.

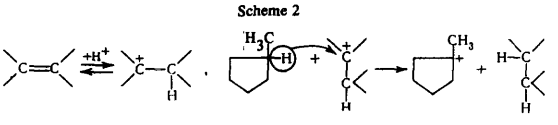
Several investigators have observed ionic hydrogenation as a side reaction in the study of the alkylation and the polymerisation of alkenes [1-3]. Nametkin and Abakumovskaya [4] as early as 1932 probably observed ionic hydrogenation by the action of sulphuric acid on cyclohexene. From the reaction products they isolated a hydrogenated dimer, obviously formed by interaction between the carbonium ion (formed by protonation of cyclohexene) and another cyclohexene molecule acting as a donor of a hydride ion.

Ipatieff and Pines [5-7], in an attempt to alkylate alkylbenzenes with alkenes in sulphuric or hydrofluoric acid, obtained good yields of alkanes (Scheme 1). In the above cases and in the work of Haaf and Koch [8] (Scheme 2) the proton donor was sulphuric or hydrofluoric acid, while the donor of a hydride ion was an alkane or an alkylbenzene.

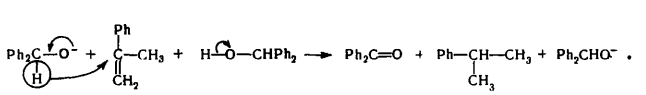
Scheme 1



Scheme 2



Vitt and Martinkova [9] effected a reaction closely similar to ionic hydrogenation on reducing the activated double bond in methylstyrene with diphenylmethanol and its alkoxide:



In contrast to the reactions considered earlier, in which the intermediate formation of carbonium ions is either demonstrable or extremely probable, it is difficult to assume such formation in the present reaction. Hydrogenation apparently takes place by a different mechanism in this case.

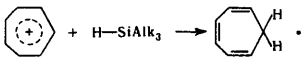
In ionic hydrogenation it is necessary that the proton donor should be sufficiently active to form a carbonium ion, but its activity should be limited, since it must not react with the hydride-ion donor to form molecular hydrogen. Besides, the carbonium ion should possess a certain stability, so that its lifetime is sufficient for

reaction with the hydride-ion donor. Yet increase in stability of the carbonium ion diminishes its rate of interaction also with the hydride donor, so that a more active source of hydride ions may be required in conducting the reaction. Ionic hydrogenation will yield only one product provided that the rate of interaction of the carbonium ion with the hydride-ion donor exceeds the rates of isomerisation and polymerisation of the carbonium ion.

It follows from the above that the choice of pair of hydrogenating agents is of decisive significance. Kursanov, Parnes, and their coworkers proposed trifluoroacetic acid and a trialkylsilane as a hydrogenating pair. These compounds hardly interact at all. Trifluoroacetic acid is a strong acid ($H_0 = -3.2$) having strong ionising and solvating properties [10]. The ability of alkyl- and aryl-silanes to split off a hydride ion has now been proved. The hydride activity of the hydrogen in a silane was already evident from the work of Whitmore, Pietrusza, and Sommer [11], who found that neopentyl chloride reacts with triethylsilane in the presence of aluminium chloride, being converted into isopentane:

$$(CH_3)_3CCH_2Cl + H{-}SiEt_3 \xrightarrow{AlCl_3} (CH_3)_3CHCH_2CH_3 .$$

More recent work has shown that a trialkylsilane transforms the tropylium ion into cycloheptatriene [12]:



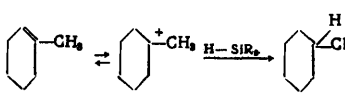
Corey and West [13] studied the exchange of hydrogen for halogen in a silane–triphenylmethyl halide system, and showed that the reaction occurs in those polar solvents in which the carbon–halogen bond undergoes dissociation (nitromethane, nitrobenzene, and dichloroethane), but not in non-polar solvents, in which dissociation is not observed. Diphenylmethyl halides and t-butyl chloride do not react with a silane. On the addition of boron tribromide to the reaction mixture, however, reaction takes place, in conformity with results for the dissociation of t-butyl chloride in the presence of boron tribromide [14].

Kursanov, Setkina, and Novikov [15] have established that phenylsilanes are capable of the ionic exchange of hydrogen with lithium tetradeuterioaluminate. Since lithium tetrahydroaluminate is a strong hydride-ion donor, the occurrence of hydrogen exchange is evidence of the hydride activity of the hydrogen in silanes.

II. IONIC HYDROGENATION OF HYDROCARBONS

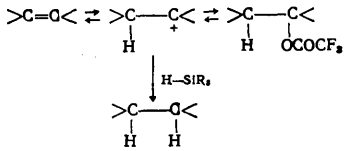
1. Alkenes

(*a*) Monoalkenes. Investigations have shown [16,17] that, with relative proportions of the components—alkene, triethylsilane, and trifluoroacetic acid—of 1 : 1 : 2 at 20–50°C, selective hydrogenation takes place of those alkenes in which branching occurs at the ethylenic carbon (such as methylcyclohexene, methylcyclopentene, 2-methylbut-2-ene, 2-methylpent-1-ene, etc.), saturated hydrocarbons being formed in 80% yield:



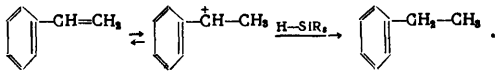
Unbranched alkenes and cycloalkenes, as well as alkenes in which there is no branching at the ethylenic carbon, are not hydrogenated.

This reaction was explained on the basis that ionic hydrogenation is undergone only by alkenes which, as a result of the protonation or dissociation of the corresponding trifluoroacetate, are able to form a sufficiently stable carbonium ion:

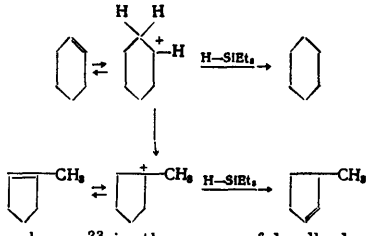


In a study of the isotopic exchange of hydrogen Setkina and Kursanov showed [18–21] that trifluoroacetates of secondary alcohols, unlike those of tertiary alcohols, do not form carbonium ions in trifluoroacetic acid. It was found, in full agreement with this, that, under the conditions of ionic hydrogenation, the trifluoroacetate of a tertiary alcohol reacts with a silane in trifluoroacetic acid (with equimolecular proportions of the components) to form a saturated hydrocarbon [16]. The trifluoroacetate of a secondary alcohol does not react with the silane under these conditions.

The fact that styrene, in which there is no branching at an ethylenic carbon atom, is hydrogenated to ethylbenzene is formally inconsistent with the above scheme. However, such behaviour of styrene is apparently due to the formation by its protonation of a carbonium ion which is stabilised by conjugation with the benzene ring †:



Similar behaviour is shown by indene ‡ and vinylcyclopropane [22], which on protonation also give carbonium ions, stabilised by the benzene ring and by the cyclopropane ring respectively. Further support for the scheme is provided by the slow ionic hydrogenation of unbranched alkenes and cycloalkenes when the acidity (the relative quantity of trifluoroacetic acid) is increased or when the reaction is conducted under more severe conditions (heating in sealed tubes at 140°C). Under these conditions, however, isomerisation products are also formed, and the yield of saturated hydrocarbons is very low.



It has been shown [23] in the case of 1-alkylcyclohexenes that the yield and the rate of ionic hydrogenation are independent of the number of atoms in the alkyl group.

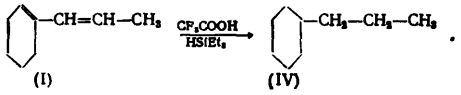
The fact that unbranched alkenes and cycloalkenes undergo ionic hydrogenation with increase in the acidity of the medium agrees well with results obtained by Setkina, Kursanov, and their coworkers [21], who have shown that the formation of a carbonium ion from trifluoroacetates depends on the acidity of the medium.

† It must be noted that the yield of ethylbenzene is small (~ 30%) in the case of styrene, probably because of the competitive effect of polymerisation.

‡ Indene polymerises under the reaction conditions, so that its yield is small.

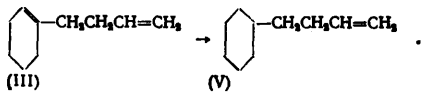
(*b*) Dienes. Various 1-alkenylcyclohexenes—1-propenylcyclohexene (I), 1-allylcyclohexene (II), and 1-but-3′-enylcyclohexene (III)—have been investigated[23] in studying the behaviour of dienes under conditions of ionic hydrogenation, when only one of the ethylenic bonds is able to yield a tertiary carbonium ion on protonation.

Propenylcyclohexene, which contains conjugated double bonds, is completely hydrogenated to propylcyclohexane (IV):



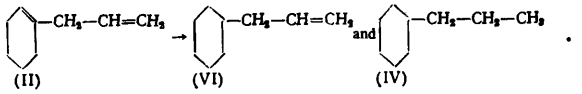
(I) (IV)

In 1-but-3′-enylcyclohexene (III), in which the multiple bonds are separated by two carbon atoms, only the branched ethylenic bond is hydrogenated, with the formation of but-3-enylcyclohexane (V):



(III) (V)

In the case of 1-allylcyclohexene (II), where the multiple bonds are separated by a single carbon atom, two hydrogenation products—allylcyclohexane (VI) and propylcyclohexane (IV)—are formed in the proportions 4 : 1 (see Table 1):



(II) (VI) (IV)

Table 1. Ionic hydrogenation of dienes (at 50°C for 10 h).

Initial alkene	Reaction product	Yield (%) with proportions of alkene : silane : acid	
		1:1:2	1:2:3
1-Propenylcyclohexene	propylcyclohexane	35	70
1-Allylcyclohexene	allylcyclohexane,	28	55
	propylcyclohexane	7	15
1-But-3′-enylcyclohexene	but-3-enylcyclohexane	30	65
Cyclohexadiene	cyclohexene	<2	

The formation of propylcyclohexane from allylcyclohexene may, perhaps, be explained by partial isomerisation of the latter, in the presence of trifluoroacetic acid, into propenylcyclohexene, which has been shown to be completely hydrogenated to propylcyclohexane.

Conjugated dienes containing no branchings undergo hardly any ionic hydrogenation. Under the reaction conditions cyclohexa-1,3-diene gives cyclohexene in less than 2% yield.

2. Aromatic Hydrocarbons

Trifluoroacetic acid and triethylsilane convert anthracene into 9,10-dihydroanthracene[24]. In benzene solution, with the hydrocarbon, silane, and acid in the proportions 1 : 1 : 3.5, the yield of dihydroanthracene at 50°C is 80% after 10 h. Benzene and naphthalene do not react even under considerably more severe conditions.

3. Cyclopropane Hydrocarbons

Cyclopropanes behave similarly to alkenes in many reactions[25]. In particular, they are able to form salts of carbonium ions on treatment with acids. They might therefore be expected to undergo ionic hydrogenation, and obey the same rules as alkenes.

It has in fact been shown[22] that *gem*-dimethylcyclopropanes are hydrogenated with cleavage of the ring to form saturated hydrocarbons (in yields up to 80%). Ethylcyclopropane does not undergo ionic hydrogenation. Phenylcyclopropane is hydrogenated to n-propylbenzene (in 70% yield) (see Table 2).

Table 2. Ionic hydrogenation of cyclopropane hydrocarbons.

Substituents in cyclopropane	Hydrocarbons obtained	Yield, %
1,1,2-Trimethyl	2,3-dimethylbutane,	75
	2-methylpentane	25
Phenyl	propylbenzene	70
Isopropyl	2-methylpentane	40

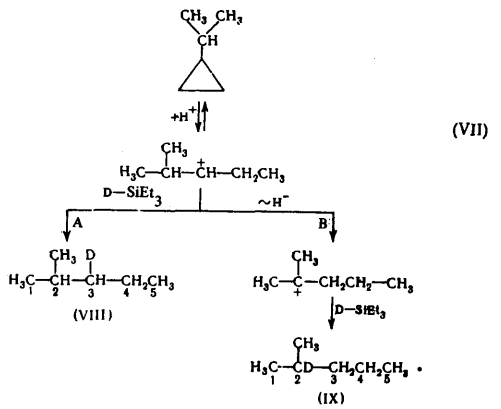
First of all it was necessary to establish the site of ring cleavage during ionic hydrogenation. It was found that the bond between the most and the least hydrogenated carbon atoms ruptures preferentially, as occurs in the action of mercury acetate and inorganic acids[26,27].

It is interesting that, in heterogeneous hydrogenation on palladium, the bond between the two most hydrogenated carbon atoms breaks[28], which leads to the formation of hydrocarbons isomeric with those obtained by ionic hydrogenation.

Isopropylcyclopropane also can be hydrogenated under these conditions, although protonation cannot lead directly to the formation of a tertiary carbonium ion. The capacity of isopropylcyclopropane for ionic hydrogenation may be due to the formation in this case, as an exception to the general rule, of a secondary carbonium ion, which reacts with the silicon hydride to give an alkane. However, the reaction could also occur in a different way, intramolecular hydride transfer producing isomerisation with formation of a tertiary carbonium ion, which reacts with the silane.

To settle this question a study has been made[29] of the reaction of isopropylcyclopropane (VII) with trifluoroacetic acid and deuteriotriethylsilane. If the secondary carbonium ion reacts with the silane, the 2-methylpentane formed by the reaction should contain deuterium in position 3 (VIII) (path A). If, however, a tertiary carbonium

ion reacts with the silane, the deuterium should be located in position 2 (IX) (path B):



(VII)

(VIII)

(IX)

Analysis of the proton magnetic resonance spectra has shown unambiguously that the deuterium is in position 2, which indicates that hydrogenation takes place by path B.

The ionic hydrogenation of isopropylcyclopropane is peculiar in occurring approximately to the extent of 40%, this yield not increasing with the duration of the experiment[30]. The formation of 2-methylpentane is accompanied by that of 1-ethyl-2-methylpropyl trifluoroacetate $CH_3CH(CH_3)CH(C_2H_5)OCOCF_3$. These results can be understood on the assumption that the cyclopropane ring is not opened in the first act of protonation, but a protonated cyclopropane is formed, the possibility of which in the first stage is widely accepted at the present time[31-33]. The protonated cyclopropane then undergoes cleavage, with the irreversible formation of the trifluoroacetate of the secondary alcohol. Partial isomerisation occurs at the same time as ring cleavage, and yields a tertiary carbonium ion, which reacts with the silane to give 2-methylpentane.

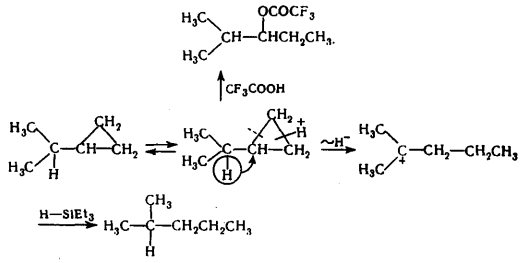


Table 3. Comparative results for the ionic hydrogenation of unsymmetrical trimethylcyclopropane and of 2,3-dimethylbut-2-ene.

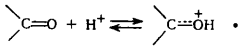
Hydrocarbon	Tim, h			
	1	3	6	12
1,1,2-Trimethylcyclopropane	27	32	49	65
2,3-Dimethylbut-2-ene	20	38	45	67

The rates of hydrogenation of 1,1,2-trimethylcyclopropane and of 2-methylpent-1-ene are approximately the same[29].

It is interesting to compare these data with results obtained by Peterson[34], who has found that butylcyclopropane reacts 300 times as rapidly as hex-2-ene with trifluoroacetic acid. From this he concludes that cyclopropane hydrocarbons react more rapidly than the corresponding alkenes with this acid. If this conclusion is regarded as generally applicable, our results indicate that protonation is not the rate-determining stage in the ionic hydrogenation of cyclopropanes.

III. IONIC HYDROGENATION OF THE CARBONYL GROUP

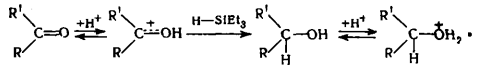
In acid media the carbonyl group in ketones and aldehydes is capable of protonation, the following equilibrium being established in the solutions:



Hydride transfer with formation of the alcohol might be expected to occur on addition of a hydride-ion donor to the reaction mixture. Ionic hydrogenation of the carbonyl group in ketones and aldehydes on treatment with trifluoroacetic acid and a silane is in fact observed. However, the composition of the reaction products depends on the structure of the initial ketones and aldehydes.

1. Ketones

Under conditions of ionic hydrogenation aliphatic ketones[35] (acetone, butan-2-one, cyclohexanone, phenylpropan-2-one) give a mixture of the alcohol and its trifluoroacetate. Aromatic and aliphatic–aromatic ketones (acetophenone, benzophenone, pentamethylacetophenone, Michler's ketone), however, undergo further reduction, the reaction product being a hydrocarbon. This difference in behaviour between aliphatic and aromatic ketones is easily explained by means of the general reaction scheme:



If R′ = Ar, further change is possible:

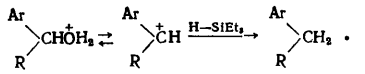


Table 4. Ionic hydrogenation of ketones.

Ketone	Ketone : silane : acid	Time, h	Yield, %	
			alcohol + trifluoroacetate	hydrocarbon
Butan-2-one	1:1.5:3	10	80	—
Cyclohexanone	1:1:2	10	55	—
Cyclohexanone	1:2.5:2	20	75	—
Acetophenone	1:2.5:2	10	—	70
Benzophenone	1:2.5:2	15	—	94

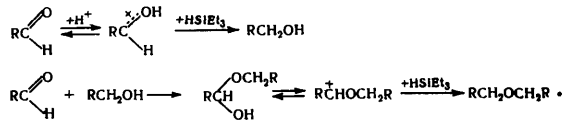
Protonation of the resulting alcohol followed by elimination of water may lead to the formation of secondary carbonium ions. In the case of aromatic and aliphatic–aromatic ketones, however, the carbonium ion is stabilised by the adjacent benzene ring(s). Such a carbonium ion is shown by the ionic hydrogenation of styrene[17] to react with a

silane to form a hydrocarbon. Similarly, the hydrogenation of cyclopropyl methyl ketone results in the formation of ethylcyclopropane and *trans*-pentene, the latter of which has been shown earlier to appear in attempts at the ionic hydrogenation of ethylcyclopropane.

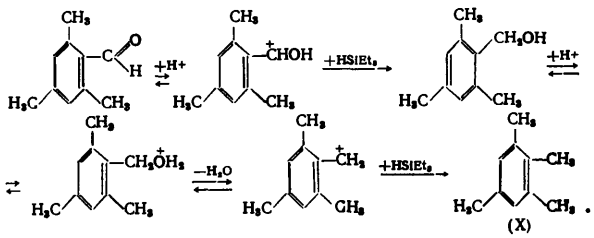
The introduction of electron-acceptor substituents into the benzene ring of an aromatic ketone should diminish the reaction velocity. In fact, Michler's ketone forms bis-*p*-dimethylaminophenylmethane in 75% yield after being heated with a large excess of acid at 80°C for 40 h, whereas benzophenone is converted into diphenylmethane at 55°C almost completely after 15–20 h.

2. Aldehydes

Aldehydes react extraordinarily rapidly with triethylsilane in trifluoroacetic acid to form a mixture of an ether and an alcohol (and the trifluoroacetate of the latter)[36], the amounts of ether and alcohol being approximately the same in the case of aliphatic aldehydes, whereas aromatic aldehydes are almost entirely converted into ethers (e.g. benzaldehyde gives 80% of dibenzyl ether immediately the reactants are mixed). Such a result cannot be explained by condensation of alcohol formed in the first stage, since in trifluoroacetic acid alcohols form little or no ether at all. Moreover, conducting the ionic hydrogenation of an aldehyde in the presence of an alcohol having a different hydrocarbon radical yields an unsymmetrical ether. These facts suggest that production of the ether involves the intermediate formation of a hemiacetal:



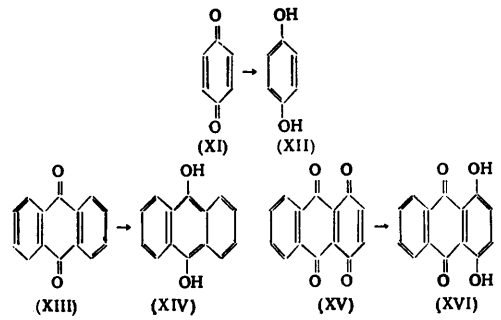
The benzyl cation might be expected to be stable, so that its lifetime would be sufficient for reaction with the silane, and consequently the ionic hydrogenation of benzaldehyde would yield toluene. However, it has been shown[36] that toluene is not formed under these conditions. Hanazaki and Nagakura[37] showed that the stability of the 2,4,6-trimethylbenzyl cation is comparable with that of the α-methylbenzyl cation, which is formed by the protonation of acetophenone. From this it could be expected that 1,2,3,5-tetramethylbenzene would be formed by the ionic hydrogenation of 2,4,6-trimethylbenzaldehyde. In fact, this hydrocarbon (X) is formed under these conditions in 70% yield:



(X)

3. Quinones and αβ-Unsaturated Ketones

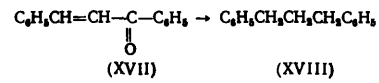
It was of interest to ascertain the mutual influence of carbon–carbon and carbon–oxygen multiple bonds conjugated with one another. The first compounds chosen for investigation were quinones[38]. Study of the ionic hydrogenation of quinones has shown that benzoquinone (XI) is converted into quinol (XII), anthraquinone (XIII) into anthraquinol (XIV), and anthra-1,4:9,10-diquinone (XV) into quinizarin (XVI):



(XI) (XII) (XIII) (XIV) (XV) (XVI)

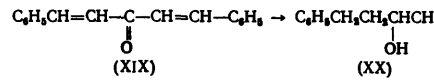
It is interesting that the resulting quinizarin does not undergo further ionic hydrogenation either on prolonged heating of the mixture or on the addition of trifluoroacetic acid.

The ionic hydrogenation of 1,3-diphenylpropenone (XVII) leads to the formation of 1,3-diphenylpropane (XVIII) in 80% yield:



(XVII) (XVIII)

The hydrogenation of 1,5-diphenylpenta-1,4-dien-3-one (XIX) gives 1,5-diphenylpentan-3-ol (XX) as the main product[39]:



(XIX) (XX)

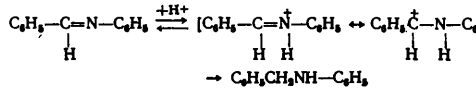
4. Carboxylic Acids

The carbonyl group in carboxylic acids and esters does not undergo ionic hydrogenation.

IV. IONIC HYDROGENATION OF A C=N BOND

The electronic structures of the C=N and C=O bonds have much in common, this being responsible for the similarity in their chemical properties, apparent especially in addition reactions. From this it could be supposed that azomethines would undergo ionic hydrogenation to form amines.

It has in fact been found[40] that benzylideneaniline and *o*- and *p*-benzylidenetoluidines react with triethylsilane and trifluoroacetic acid. With molar proportions of anil, silane, and acid of 1:1:3 at 60–70°C the amines are formed in yields respectively of 78%, 86%, and 95% after 60 min.



In contrast to the above anils, cyclohexylidene-*o*-toluidine does not form an amine under these conditions. The reason for such behaviour requires further study.

V. IONIC HYDROGENOLYSIS

The fact that cyclopropane hydrocarbons containing no multiple bonds undergo ionic hydrogenation enables us to hope that certain single bonds may be hydrogenated under these conditions. Compounds containing an atom having a lone pair of electrons were chosen to test this hypothesis. Addition of a proton produces a cation. If then a bond is ruptured with formation of a new cation, it is in principle possible for this to interact with a hydride-ion donor. The concentration of this cation must be sufficient for such interaction to occur. The first class of such compounds to be studied was the disulphides.

Table 5. Ionic hydrogenolysis of disulphides.

Disulphide	Yield of thiol, %
$(t\text{-}C_4H_9)_2S_2$	67
$(C_6H_5)_2S_2$	45
$(4\text{-}CH_3OC_6H_4)_2S_2$	73.5
$(2\text{-}NO_2C_6H_4)_2S_2$	0
$[2,4\text{-}(NO_2)_2C_6H_3]_2S_2$	0

1. The S–S Bond

Disulphides have been found[41] to interact with trifluoroacetic acid and triethylsilane, the S–S bond being cleaved and hydrogenated to form the corresponding thiols as the sole products of the reaction. Unchanged disulphide was isolated.

Table 6. Interaction of sulphenyl chlorides with triethylsilane.

Sulphenyl chloride	Solvent	Reaction product (yield, %)	Sulphenyl chloride	Solvent	Reaction product (yield, %)
C_6H_5SCl	none	disulphide (95)	$2\text{-}NO_2\text{-}4\text{-}ClC_6H_3SCl$	CF_3COOH	disulphide (65), thiol (30)
C_6H_5SCl	hexane	disulphide (slow reaction)	$4\text{-}NO_2C_6H_4SCl$	hexane	disulphide (slow reaction)
S_2Cl_2	none	no reaction			
S_2Cl_2	CF_3COOH	S, $CF_3COOSiEt_3$			
$2\text{-}NO_2C_6H_4SCl$	CCl_4	no reaction	$4\text{-}NO_2C_6H_4SCl$	CF_3COOH	disulphide (98)
$2\text{-}NO_2C_6H_4SCl$	HCOOH	disulphide (quantitative)	$2,4\text{-}(NO_2)_2C_6H_3SCl$	CF_3COOH	no reaction
$2\text{-}NO_2C_6H_4SCl$	CF_3COOH	disulphide (76), thiol (18)			

Separate experiments had shown that trifluoroacetic acid does not visibly react with a disulphide in the absence of a silane, and in the absence of the acid the silane does not react with the disulphide.

The scheme

$$RSSR + CF_3COOH \rightleftarrows RSH + [RS]^+CF_3COO^-$$
$$[RS]^+CF_3COO^- + H{-}SiEt_3 \rightarrow RSH + (SiEt_3)OCOCF_3$$
$$RSSR + H{-}SiEt_3 + CF_3COOH \rightarrow 2RSH + CF_3COOSiEt_3$$

was proposed for the reaction. It is supported by the fact that sulphenyl chlorides, which are potential sources of the sulphenium ion[42], react with triethylsilane under mild conditions, to give a theoretical yield of reduction products[43] (see Table 6). The general scheme of the reaction is

$$RSCl \overset{+H^+}{\rightleftarrows} [RS]^+ + HCl;\ [RS]^+ + H{-}SiEt_3 + CF_3COOH \rightarrow$$
$$\rightarrow RSH + CF_3COOSiEt_3;\quad RSH + RSCl \rightarrow RSSR + HCl\ .$$

Formation of the thiol precedes that of the disulphide, since nitro-disulphides do not react with the silane in trifluoroacetic acid (Table 5). The fact that a thiol results from the reaction means that its rate of formation exceeds the rate of interaction with the initial sulphenyl chloride.

Table 5 shows that electron-donor substituents increase the yield of thiols, whereas electron-acceptor substituents prevent the reaction. Increase in acidity raises the yield of thiol. This is consistent with the view that the first act in the reaction is protonation, leading to rupture of the S–S bond. It is noteworthy that the interaction of sulphenyl chlorides with trifluoroacetic acid and a silane involves hydrogenation of the S–Cl single bond with the formation of HCl and HSR.

2. The C–O Bond

It has already been noted that aromatic and aliphatic–aromatic alcohols undergo ionic hydrogenation of the C–O bond to form a hydrocarbon and water. Results obtained for the ionic hydrogenation of ketones and aldehydes show that ethers do not undergo this reaction under mild conditions. With a large (tenfold) excess of trifluoroacetic acid, however, certain ethers are able to react with a silane to form a hydrocarbon[44].

Table 7. Ionic hydrogenolysis of ethers.

Ether	Hydrocarbon	Yield, %
$t\text{-}C_4H_9OC_2H_5$	$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_3$	60
$(C_6H_5)_2CHOCH(C_6H_5)_2$	$C_6H_5CH_2C_6H_5$	60
$C_6H_5CH_2OC_2H_5$	$C_6H_5CH_3$	7
$C_6H_5CH_2OCH_2C_6H_5$	$C_6H_5CH_3$	3

Table 7 indicates that ionic hydrogenation occurs with those ethers which, on protonation followed by rupture of the C–O bond, are capable of forming a relatively stable carbonium ion. The hydrogenolysis of an ether can be represented by the following scheme

$$ROR' \overset{+H^+}{\rightleftarrows} \underset{\displaystyle H}{\overset{+}{\underset{|}{R}}}OR' \rightarrow ROH + R'^+$$
$$R'^+ + H{-}SiEt_3 \rightarrow R'H\ .$$

VI. MECHANISM OF IONIC HYDROGENATION

The ionic hydrogenation of a multiple bond comprises two acts—addition of a proton to form a cation and transfer to the latter of a hydride ion to form the hydrogenation product—the relative rates of which depend on the structure of the reactants. The sequence of the acts may even be reversed as a consequence of this structure. Such a

reaction was reported by Knunyants, Cheburkov, and Aronov [45], who hydrogenated perfluoro-2,4-dimethylpenta-2,3-diene by the action of hydrogen sulphide and sodium hydrogen sulphide in sulpholan. These workers considered it probable that the first act in the reaction was the removal by the allene of a hydride ion from the hydrosulphide, followed by addition of a proton from the hydrogen sulphide:

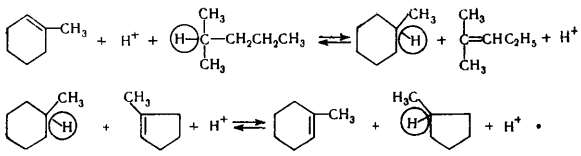
$$(CF_3)_2C{=}C{=}C(CF_3)_2 \xrightarrow[\text{sulpholan}]{H_2S+NaHS} (CF_3)_2CHCH{=}C(CF_3)_2 + S \ .$$

It is quite obvious that triethylsilane is not the only possible hydride-ion donor in ionic hydrogenation, just as trifluoroacetic acid is not the sole possible donor of protons.

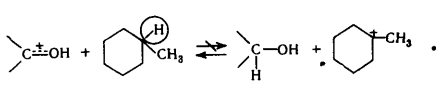
1. Donors of Hydride Ions

In the consideration of possible hydride-donors it must be borne in mind that the less stable a carbonium ion the more active it is as a hydride-ion acceptor but the shorter its lifetime (or the less probable its formation in a kinetically free state). And conversely, the more stable carbonium ions live longer, but are less active. Compounds which can act as hydride-ion donors in other reactions are of interest for use as possible donors of hydride ions in ionic hydrogenation. Examples of such compounds are saturated hydrocarbons containing a tertiary carbon atom. Their ability to act as hydride-ion donors has been demonstrated by Ipatieff and Pines [5-7], Haaf and Koch [8], Kramer [46], and Setkina et al. [47].

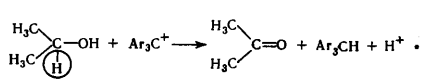
A mixture of four hydrocarbons—methylcyclohexene, methylcyclohexane, 2-methylpentane, and 2-methylpent-2-ene—was isolated from the reaction between methylcyclohexene and 2-methylpentane in trifluoroacetic acid. Similarly, the interaction between methylcyclopentene and methylcyclohexane in trifluoroacetic acid yielded a mixture of methylcyclopentene, methylcyclopentane, methylcyclohexane, and methylcyclohexene:



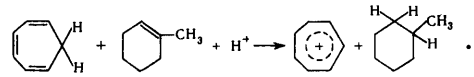
However, it has proved impossible to use a hydrocarbon containing a tertiary carbon atom as a hydride-ion donor to hydrogenate the carbonyl group. The apparent explanation is that the carboxonium ion is too stable to detach a hydride ion from the hydrocarbon, while the tertiary carbonium ion which should result is less stable. Since no reaction takes place between a hydrocarbon containing a tertiary carbon atom and a protonated ketone, it might be expected that the reverse reaction between an alcohol and a tertiary carbonium ion would occur:



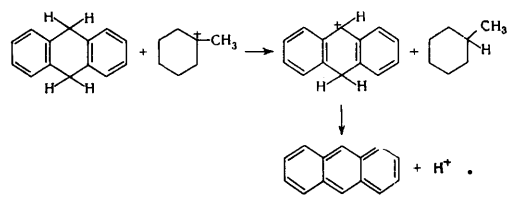
Actually, the reaction discovered by Bartlett [48] between an aliphatic alcohol and a triarylmethanol in sulphuric acid is in effect a reaction between an alcohol and a carbonium ion:



We have studied cycloheptatriene as another hydride-ion donor in ionic hydrogenation. The ability of cycloheptatriene to donate a hydride ion is due to the fact that the stable aromatic ion tropylium is thereby formed. Cycloheptatriene has been used as a hydride-ion donor in various reactions by Kursanov and Vol'pin [49], Dauben [50], Volz [51], and other workers [52]. It has been found [16,17] to react with methylcyclohexene in trifluoroacetic acid to form methylcyclohexane. Owing to competition by the polymerisation of cycloheptatriene in acid medium, however, the yield of the saturated hydrocarbon is low (~5%):



9,10-Dihydroanthracene proved to be a good hydride-ion donor in ionic hydrogenation. Its ability to donate a hydride ion was demonstrated by Braude and Linstead [53], Bonthron and Reid [54], and Nenitzescu and Balaban [55]. Kursanov, Parnes, and Bolestova [24] have found that 9,10-dihydroanthracene is able to give up a hydride ion to methylcyclohexene protonated with trifluoroacetic acid. This results in the formation of anthracene and methylcyclohexane (yield 70%):



The use of dihydroanthracene as a hydride-ion donor has enabled a stronger acid than trifluoroacetic to be used, which is impossible with triethylsilane, since the latter reacts with strong acids with the evolution of hydrogen.

An attempt to use acenaphthene as hydride-ion donor has shown merely the theoretical possibility of such a reaction, since the yield of saturated hydrocarbon is very small.

It follows from the above results that various hydride-ion donors can be employed in the ionic hydrogenation of alkenes, but so far the best results have been achieved with trialkylsilanes and 9,10-dihydroanthracene.

Methyldiethylsilane and mono-, di-, and tri-phenylsilanes have also been used as hydride-ion donors. In the series of phenylated silanes the ability to transfer a hydride ion diminishes in the sequence $(C_6H_5)_2SiH_2 > C_6H_5SiH_3 > (C_6H_5)_3SiH$ [17]. A similar relationship had been established earlier by Kursanov, Setkina, and Novikov [15].

2. Donors of Protons

Trifluoroacetic acid has been used as proton donor in ionic hydrogenation because, while being a strong acid ($H_0 = -3.2$), it possesses great ionising and solvating power [10]. Study of the effect of the quantity of acid on the yield of alkane has shown that the reaction takes place only in the presence of excess of acid, and is strongly accelerated by increase in this excess.

With a hundredfold excess of acid, isomerisation also becomes appreciable, this being absent when smaller quantities of trifluoroacetic acid are used. The work of Kursanov and Setkina [18-21] on the isotopic exchange of hydrogen in trifluoroacetates has shown the influence of acidity on the formation of carbonium ions from trifluoroacetates. These workers have established that the rate of

formation of carbonium ions is equal to the rate of formation of alkenes. It has also been found that, with $H_0 = -3.2$, trifluoroacetates of tertiary alcohols form carbonium ions. Those of secondary alcohols do not undergo heterolysis at this acidity, and carbonium ions are not formed. With increase in acidity, however, secondary carbonium ions are, nevertheless, formed.

Table 8. Effect of quantity of trifluoroacetic acid on yield of methylcyclohexane.

Molar ratio of acid to methylcyclohexene	Yield of methylcyclohexane, %	Duration of expt., h
1	4	120
2	73	120
10	78	1
100	80	0.3

3. Mechanism of the Hydride Migration

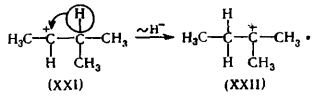
Hypotheses on the intramolecular and intermolecular transfer of a hydride ion were put forward long ago, but their proof encountered considerable difficulties because the hydride-ion acceptor was most often an unstable carbonium ion, the appearance of which during the reaction was very difficult to establish.

The hypothesis of hydride migration would appear to be inconsistent with the absence of molecular hydrogen evolution when the reaction is conducted in acid medium. Actually, in this case it would be necessary to expect that gaseous hydrogen would be produced by the process

$$H^- + H^+ \rightarrow H_2 .$$

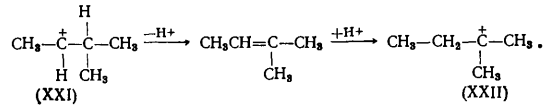
However, this discrepancy can be explained on the assumption that hydride migration takes place without the formation of a kinetically independent hydride ion, the transfer of a hydride ion taking place directly from molecule to molecule (or ion). In fact, a sufficiently active acceptor should be present to detach a hydride ion from a molecule. The solvated proton of an acid may not possess the required activity, so that it will not react with the hydride-ion donor and molecular hydrogen will not be formed. However, it is then impossible to check the act of hydride-ion transfer, which may involve the proton and the two electrons migrating in either one or more steps.

The question of the mechanism of the act of hydride-ion transfer is part of the general problem of establishing the mechanism of nucleophilic substitution. Just as the latter can be regarded as occurring in two steps (an electron, followed by an atom), hydride transfer can be divided into two steps (electron and hydrogen atom). However, whether hydride migration actually takes place in two steps, and if so in what cases, will be shown by future research. It must be stressed that the question of whether hydride transfer takes place in one or two stages is a matter of the relative rates of these steps. If the rate of the second step—transfer of a hydrogen atom to an already formed radical—considerably exceeds the rate of the first step, this is identical for chemical reactions to a one-step hydride transfer:



(XXI) (XXII)

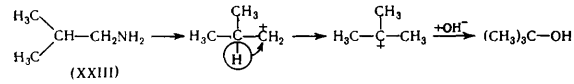
However, the same result will be achieved if the carbonium ion (XXI), having lost a proton, is converted into an alkene, which adds a proton from the medium to form a tertiary carbonium ion (XXII):



(XXI) (XXII)

Cannell and Taft showed[56] that under certain conditions the isomerisation of a carbonium ion cannot be explained by the intermediate formation of an alkene. They studied the deamination of isobutylamine (XXIII) by the action of nitrous acid in a medium containing deuterium oxide. The main reaction product was t-butyl alcohol: i.e. the initially formed isobutyl cation had rearranged to a t-butyl cation. If isomerisation occurred as a result of intramolecular hydride transfer (Scheme 3), the t-butyl alcohol formed should not contain deuterium bound to carbon. If, on the other hand, isomerisation were a consequence of the reversible formation of an alkene (Scheme 4), the t-butyl alcohol should contain deuterium bound to carbon (XXIV).

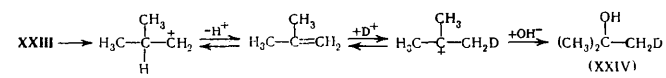
Scheme 3



(XXIII)

It was found that, if the reaction is conducted at pH > 3 and 38°C, the t-butyl alcohol will not contain deuterium bound to carbon. Since alkenes (but-1-ene, but-2-ene, isobutene) are formed as well as the alcohol in the reaction, it is obvious that no protonation of the alkenes takes place under the experimental conditions, isomerisation of the carbonium ion being a consequence of hydride transfer (Scheme 3). In a more acid medium, in which protonation of alkenes takes place, isomerisation of the carbonium ion will occur both as a consequence of intramolecular hydride migration and as a consequence of reversible formation of alkenes (Scheme 4).

Scheme 4



(XXIV)

From the above work it may be concluded that in any case, under certain conditions, isomerisation of the carbonium ion will occur as a result of intramolecular hydride transfer.

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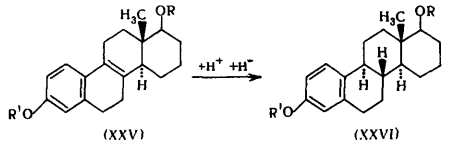
The stereochemical study of ionic hydrogenation is of great interest. Carey and Tremper have shown[57] that the ionic reduction of 1-phenyl-4-t-butylcyclohexene yields a mixture of *trans*- and *cis*-1-phenyl-4-t-butylcyclohexanes. If a disubstituted silane is used as hydride-ion donor, the *trans* : *cis* ratio is ~ 4 independently of the nature of the substituents (alkyl, aryl). If three substituents are attached to the silicon atom, this ratio is ~ 2. This fact is explained by these workers on the basis that the transition state in the *trans*-form is sterically more difficult for trisubstituted silanes. The *trans*-form is the predominant product in all cases because it is thermodynamically more favourable.

It has been shown quite recently[58] that the ionic hydrogenation of $\Delta^{8(9)}$-dehydro-D-homo-oestrogens (XXV) occurs stereospecifically to give D-homosteroids of *trans-anti-trans*-configuration (XXVI):



(XXV) (XXVI)

Thus the reaction of ionic hydrogenation is of great interest for theoretical organic chemistry, and is also a convenient method for the selective reduction of various classes of organic compounds.

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Institute of Organoelementary Compounds,
USSR Academy of Sciences, Moscow

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Derivatives of Metal Carbonyls Containing a Bond between Atoms of Transition Metals and Group IVB Elements

N.E.Kolobova, A.B.Antonova, and K.N.Anisimov

This review considers the methods of preparation, properties, and structure of organopolymetallic compounds containing elements of Group IVB connected with a metal carbonyl residue. Compounds of this type are interesting from the point of view of investigating metal-metal interaction, that is, from the theoretical point of view. Their practical use in various fields of chemistry and technology is possible. 176 references.

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I. INTRODUCTION

The intensive development of investigations in the field of the chemistry of carbonyl complexes of transition metals led to the preparation of a large number of compounds containing a direct bond between two metal atoms. Despite the fact that the existence of metal–metal bonds in organic derivatives of non-transition metals and in inorganic crystals is generally known, before 1957 no serious attention was paid to the possibility of the formation of a strong covalent bond between the atoms of transition metals in their organic derivatives—the carbonyls. It has now been found [1,2] that a metal–metal bond can be formed by all the transition metals capable of σ-bonding with carbon.

From 1962 onwards chemists have paid special attention to derivatives of metal carbonyls containing two or more covalently bonded atoms of different metals, both transition and non-transition. The present review examines the methods of preparation and properties of organopolymetallic compounds containing Group IVB elements bonded with a metal carbonyl residue. The investigation of metal–metal interaction in compounds of this type is of considerable interest both from the standpoint of the theory of the chemical bond and in view of their possible practical application.

In published reviews [1-5] dealing with the formation of covalent bonds between metal atoms, derivatives of metal carbonyls containing bonds between various transition and non-transition metals were either not considered or the consideration was limited owing to the absence of sufficient facts at the time these reviews were written.

II. STRUCTURES OF COMPOUNDS CONTAINING A BOND BETWEEN ATOMS OF TRANSITION AND NON-TRANSITION METALS

The possibility of the existence of a covalent bond between transition metal atoms was first shown in 1957 in an investigation of the structures of polynuclear metal carbonyls. Before then the only complexes (including carbonyls) known were those in which in addition to the metal–metal bond there were bridging atoms or groups between the metal atoms. The first complexes studied with metal–metal σ-bond structures were dimeric carbonyls of manganese and rhenium [6,7], or technetium [8] and molybdenum π-cyclopentadienylcarbonyl [9].

The ability of transition metals to form σ-bonds with Group IVB elements was observed [10] in 1956. Many series of compounds with chains of several covalently bound metal atoms, which can be classified as "clusters", have now been studied. According to Cotton's definition [4] "clusters" are compounds in which metal atoms are bound to one another exclusively by metal–metal bonds; this definition also includes those compounds in which not all the metals are identical. Several non-metal atoms can also be bound to the "cluster".

Since one or more $M'(CO)_5$ groups enter into most of the best studied clusters we will deal in greater detail with the molecular and electronic structure of this group.

1. Molecular Structure of the $M'(CO)_5$ Group, where M' = Mn, Tc, or Re

The structure of the $M'(CO)_5$ group was first found [6,7] in determining the structure of the dinuclear manganese carbonyl. Subsequent X-ray diffraction investigations showed that the characteristic peculiarities of this group are also kept in other compounds irrespective of the nature of the atoms or groups with which they are connected.

The metal atom in the $M'(CO)_5$ group has an octahedral configuration; five of the vertices of the octahedron are occupied by carbonyl groups and at the sixth there is a substituent X connected with the metal atom by a σ-bond. The C_{4V} symmetry of the $M'(CO)_5$ group is somewhat distorted owing to the non-linearity of the M'–C–O chains and displacement of the four equatorial CO groups to the side of the X substituent. For $Mn(CO)_5$ this displacement averages 3.8°. A possible reason for the departure from coplanarity of the equatorial CO groups is the mutual repulsion between the electrons of the axial and equatorial carbonyl groups. Another reason for the distortion of the molecule could be the intermolecular interaction due to the requirement for compact packing in the crystal lattice.

However, an electron diffraction study of the $Mn_2(CO)_{10}$ molecule showed [11] that the non-linearity of the Mn–C–O groups is also retained in the gas phase, and the oxygen atoms alternately depart to the right and left of the plane formed by the carbon atoms. Finally, rehybridisation of the d^2sp^3 orbitals of the metal atom, leading to release of energy and the strengthening of the bonds in the molecule, can be responsible for the decrease in symmetry [12].

The bonds between the metal atom and the carbonyl groups are not equivalent. In the manganese carbonyl molecule the $Mn-CO_{ax}$ distance is appreciably shorter than the bonds with the equatorial groups [11]. An analogous shortening of the M′–C bond and lengthening of the C–O bond for an axial group in comparison with the equatorial ones was observed in the molecules of $Tc_2(CO)_{10}$, [8] $HMn(CO)_5$, [13,14] $HCF{=}CFMn(CO)_5$, [15] and $HMnRe_2(CO)_{14}$. [16] Evidently this is connected with the reduction of symmetry of the electron shell along the X–M′–C–O axis, owing to the presence of substituent X (other than CO) in the trans-position to CO.

The structure of the $M'(CO)_5$ group is shown in Fig. 1. Table 1 gives the mean interatomic distances and angles between the bonds for M′ = Mn, Tc, and Re.

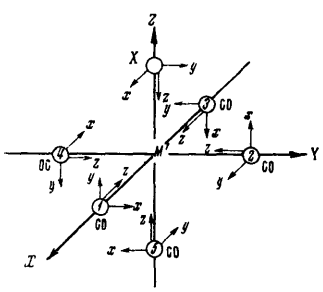


Figure 1. Structure and system of coordinates of the molecules of $XM'(CO)_5$ type.

2. Electronic Structure of Derivatives of the $XM'(CO)_5$ Type

A satisfactory description of the electronic structure of transition metal complexes is at present possible only within the framework of the LCAO-MO method. Unfortunately, there is only one theoretical investigation [17] of the nature of the bonds in the carbonyl complexes of the transition metals of Group VII and this did not include an analysis of the organopolymetallic compounds with direct metal–metal bonds.

The carbonyls of the Group VII metals are stable complexes of metals in the zerovalent state of oxidation with carbon monoxide. All the CO groups are unidentate ligands coordinated with the metal atom through carbon. Coordination by the lone pair of electrons of the carbon is preferable to that due to electrons of the oxygen atom, owing to the high electronegativity of the latter. Derivatives of metal carbonyls of the type $XM'(CO)_5$ obey Sidgwick's rule, which is reflected in the diamagnetism of compounds of this class. The metal atom acquires an inert-gas 18-electron shell by the addition to its 7 valence electrons of 10 electrons from the CO groups and the formation of an M′–X covalent bond.

As already noted above, the metal atom in the $M'(CO)_5$ group which enters into the composition of both the dimeric carbonyl and its derivatives retains the somewhat distorted octahedral configuration. According to the structural data given above and also spectroscopic [18] and kinetic investigations [19–21] the axial carbonyl group $CO_{(5)}$ (see Fig. 1) is bound to the metal atom much more strongly than each of the four equatorial groups $CO_{(1-4)}$. This shows the extensive π-bonding of the metal atom with $CO_{(5)}$. It is therefore necessary to consider three types of bond formed by the central atom with (a) the axial CO group, (b) the equatorial CO groups, (c) the ligand X.

Table 1. Mean bond lengths and valence angles in $M'(CO)_5$ groups.

Parameters of the molecules	Mn [7]	Tc [8]	Re [16]
Bond length Å			
$M'-C_{axial}$	1.792	1.899	1.86
$M'-C_{eq}$	1.840	2.000	2.005
$C-O_{axial}$	1.151	1.205	1.26
$C-O_{eq}$	1.154	1.121	1.125
Valence angles, degrees			
$M'-C-O_{axial}$	177.0±1.6	175.1±1.4	178.5±2.5
$M'-C-O_{eq}$	177.3±1.2	177.7±1.2	170.5±3.0
$C_{axial}-M-C_{eq}$	93.8±0.6	93.8±0.4	92.5±1.8
$cis\text{-}C_{eq}-M'-C_{eq}$	89.8±0.6	89.8±0.4	89.9±1.4
$trans\text{-}C_{eq}-M'-C_{eq}$	172.3±0.6	172.4±0.4	174.8±1.4

The scheme of the energy levels of the molecular orbitals for the $XM'(CO)_5$ compounds is shown in Fig. 2. [17]

(a) The bond between the metal atom and $CO_{(5)}$ has the character of σ- and π-interaction. The stable σ-bond $M'-C_{(5)}$ is the result of the combination of the s-, p_z-, and d_{z^2}-orbitals of the metal and the $2s$- and $2p$-AO's of the carbon. The π-bonding between the M′ atom and $CO_{(5)}$ is mainly effected by the interaction of the d_{xz}- and d_{yz}-orbitals of the metal with the bonding (π) and antibonding (π*) orbitals of the CO. The p_x- and p_y-orbitals of the metal can also participate to some extent in π-bonding, but they are mainly used for σ-bonding with $CO_{(1-4)}$. Hence the $M'-CO_{(5)}$ π-interaction consists of one strong bonding, one mainly non-bonding, and two antibonding MO's.

(b) The four σ-bonds of the metal with the groups $CO_{(1-4)}$ situated in the xy plane are formed as a result of the combination of the s-, d_{z^2}-, $d_{x^2-y^2}$-, p_x-, and p_y-orbitals of the metal and the $2s$- and $2p$-orbitals of carbon. Only the d_{xy}-orbital of the metal is favourable for π-bonding and the other orbitals, which have a symmetry suitable for π-bonding with $CO_{(1-4)}$ participate either, as stated above, in stronger π-bonding with $CO_{(5)}$, or in σ-bonding.

(c) The σ-bond of a metal atom with the X substituent is formed by the s-, p_z-, and partly the d_{z^2}-orbitals of the metal and the corresponding X orbitals. In addition π-bonding can also be effected between the d_{xz}- and d_{yz}-AO's of the metal and the π-orbitals of similar symmetry on substituent X. Two alternatives can be considered here: the π-donation of electrons from X to the metal atom and the dative interaction of the filled d_π-orbitals of the metal with vacant orbitals of X. In the first instance the energy of the non-bonding π-MO in the $M'-CO_{(5)}$ system is

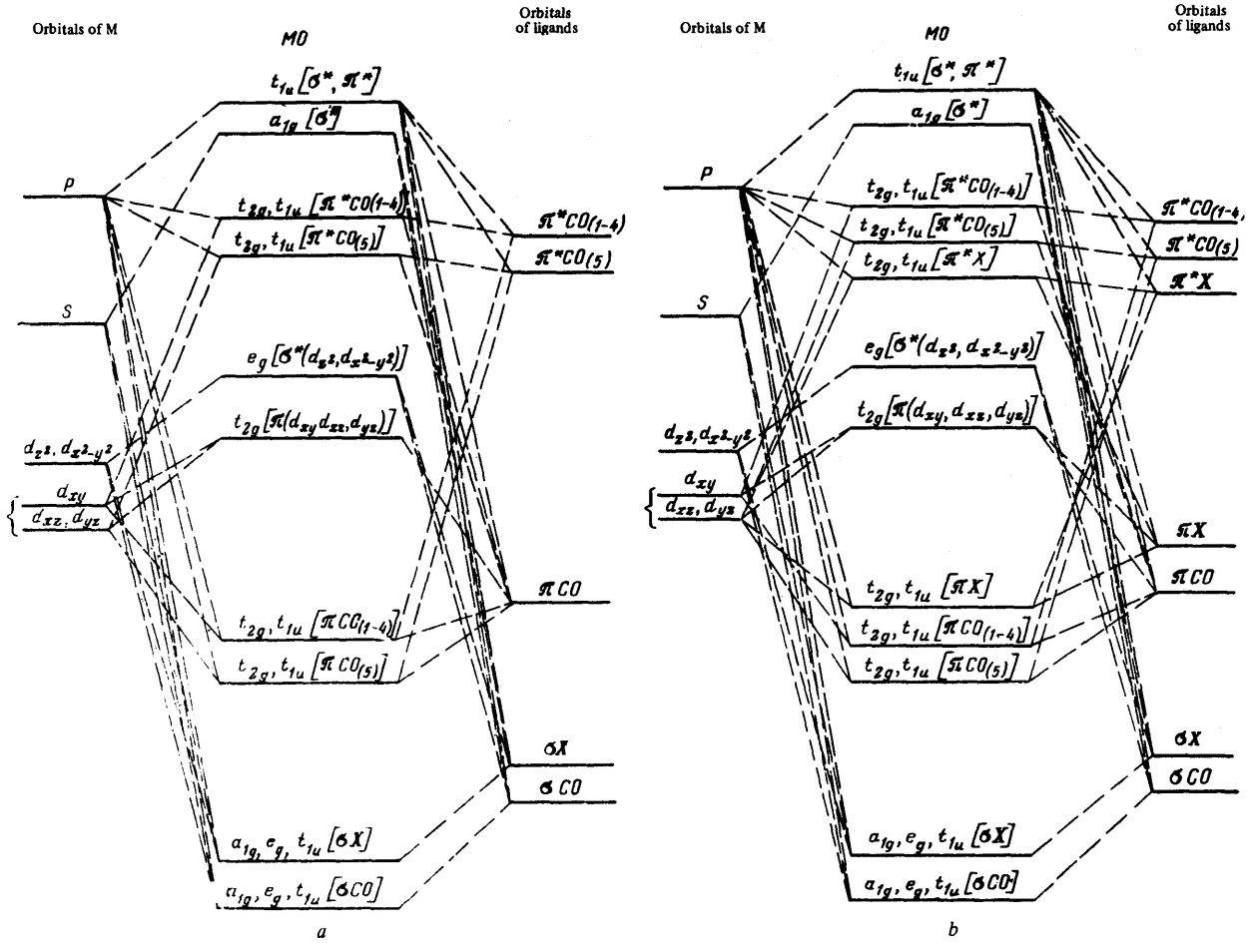


Figure 2. Scheme of energy levels for compounds of the $XM'(CO)_5$ type. *a*) X does not exhibit π-acceptor properties; *b*) X is a π-acceptor.

increased, whereas the energy of the π-orbitals of substituent X is reduced. As a result of this type of interaction additional strengthening of the $M'-CO_{(5)}$ bond should result. On the other hand, in dative π-interaction of M'–X there is competition between the π-orbitals of the ligands X and $CO_{(5)}$ for the electrons with the d_π-orbitals of the metal which should strengthen the M'–X bond and simultaneously weaken the $M'-CO_{(5)}$ bond. The scheme of the energy levels for the latter instance is shown in Fig. 2*b*.

In the diagrams the levels of the coulomb energies of the orbitals are arranged in the following order: $\sigma(CO, X) < \pi(CO) < \pi(X) < (n-1)d < ns < \pi^*(CO_{(5)}) < \pi^*(CO_{(1-4)}) < np$ in accordance with spectroscopic and kinetic results. To simplify the diagrams all the π- and π^*-orbitals of the equatorial CO-groups are shown together.

3. Structures of the Organopolymetallic Derivatives of Metal Carbonyls Containing a Metal–Metal Bond with a Group IVB Element

For the first metal carbonyl derivatives containing a Group IVB element (Si, Ge, Sn, or Pb) to be obtained it was assumed, without proof, that the two metal-containing fragments of the molecule are connected by a covalent metal–metal bond [10,22–24]. Direct proof of the covalent bonding between the atoms of the transition metal and the Group IVB element was obtained in 1964 as a result of X-ray diffraction investigation of organotin derivatives of manganese carbonyl [25,26] and it was found that in these compounds the metal–metal distance is even less than the sum of the so-called "covalent metallic radii" which is taken as the length of a single covalent bond [27].

An analysis of the compound $Ph_3SnMn(CO)_4PPh_3$ [25,28] showed that the covalently bound Sn, Mn, and P atoms are situated in a straight line, which is the principal axis of the distorted octahedron with the Mn atom at the centre; four of the vertices of the octahedron are occupied by CO groups and the other two by the tin and phosphorus atoms with approximately tetrahedral configurations. The phenyl groups at the tin and phosphorus atoms are in an eclipsed configuration relative to one another (Fig. 3). All the CO groups are somewhat displaced towards the tin atom. Table 2 gives the main parameters of the molecule.

The structures of several other derivatives of manganese carbonyl containing an Sn–Mn bond have been studied: $Ph_3SnMn(CO)_5$, [29] $Me_3SnMn(CO)_5$, [30,31] $Ph_2Sn[Mn(CO)_5]_2$, [26] $ClSn[Mn(CO)_5]_3$ [32,33] (Fig. 4*a*), and also the cluster $Ph_2Sn[Mn(CO)_5][Co(CO)_4]$, [34–36] which contains the chain Mn–Sn–CO (Fig. 4*b*). In all these molecules retention of approximately octahedral configuration of the manganese

atom and of the tetrahedral configuration of tin is observed. A comparison of the Sn–Mn internuclear distances (see Table 2) shows how sensitive the length of the metal–metal bond is to the nature of the ligands attached. One of the possible reasons for the appreciable differences in the lengths of the Sn–Mn bond could be the thermal anisotropy of the metal atoms [28]. However, the main reasons for these differences are undoubtedly of an electronic nature.

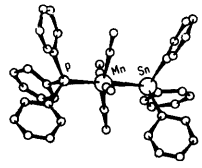


Figure 3. Structure of the $Ph_3SnMn(CO)_4PPh_3$ molecule.

In addition, purely steric factors play a large part. Thus in the series $Ph_3SnMn(CO)_5$, $Ph_2Sn[Mn(CO)_5]_2$, and $ClSn[Mn(CO)_5]_3$ as the number of $Mn(CO)_5$ groups bound to the tin atom is increased a tendency to an increase in the Sn–Mn distance is noted and the valence angles at the tin atom become increasingly distorted in comparison with the tetrahedral angles. As a result of the increase in steric hindrance the configuration of the tin atom gradually changes from tetrahedral to trigonal pyramidal.

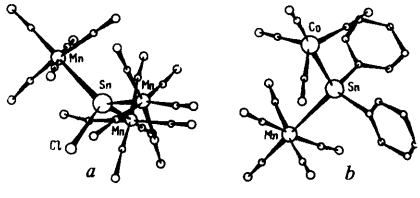


Figure 4. *a*) Structure of the $ClSn[Mn(CO)_5]_3$ molecule; *b*) structure of the $Ph_2Sn[Mn(CO)_5][Co(CO)_4]$ molecule.

The X-ray structural investigation of clusters with Sn–Fe bonds is of considerable interest both for studying the lengths of metal–metal bonds and the coordination of the metal atoms, and also for investigating the nature of the metal–ligand bonds [39–46]. It was found that in these compounds the tin atom also has approximately tetrahedral coordination with different degrees of distortion. In derivatives of iron [39–43,47,48,55] and molybdenum [43] bonded with a π-cyclopentadienyl ring the coordination of the transition metal atoms is of the "piano-stool" type characteristic of the half-sandwich compounds (Fig. 5).

The change in the nature of the metal–metal bond with the nature of the substituent at the non-transition element atom and the transfer of the electronic effects of the substituents along the metal–metal bonds can be readily traced in the series of trinuclear derivatives of the $X_2Sn[Fe(CO)_2.Cp]_2$. [39–41] As the electronegativity of X increase in the series Me < ONO < Cl there is some increase in the multiplicity of the C–O bonds, appreciable strengthening of the Sn–Fe bonds and also successive increase in the Fe–Sn–Fe angles.

Table 2. Principal structural parameters of the molecules of the carbonyl derivatives with metal–metal bonds.

Compound	M–M′ bond	Bond length, Å	Sum of "covalent" radii, Å	Mean angle between bonds, deg		Reference
$Cl_3SiCo(CO_4)$	Si—Co	2.254	2.33	Co—Si—Cl	113.3	52
				Cl—Si—Cl	105.4	
$Ph_3GeMn(CO)_5$	Ge—Mn	2.54	2.57			53
		2.60				54
$Ph_3GeRe(CO)_5$	Ge—Re	2.69	2.58			54
$Cl_3Ge[Fe(CO)_2Cp^*]_2$	Ge—Fe	2.36	2.46	Fe—Ge—Fe	128.0	47, 48
				Cl—Ge—Cl	96.0	
$Ph_3SnCr(CO)_3Cp$	Sn—Cr	2.85	2.65			54
$Ph_3SnMo(CO)_3Cp$	Sn—Mo	2.87	2.77			54
$Ph_2Sn[Mo(CO)_3Cp]_2$	Sn—Mo	2.89	2.77	Mo—Sn—Mo	116.0	54
$Ph_2Sn[W(CO)_3Cp]_2$	Sn—W	2.81	2.78	W—Sn—W	121.0	54
$Me_3SnMn(CO)_5$	Sn—Mn	2.674	2.78	Mn—Sn—C	112.2	30, 31
				C—Sn—C	107.4	
$Ph_3SnMn(CO)_5$	Sn—Mn	2.674	2.78	Mn—Sn—C	112.7	29
				C—Sn—C	106.0	
$Ph_3SnMn(CO)_4PPh_3$	Sn—Mn	2.627	2.78	Mn—Sn—C	114.2	25, 28
				C—Sn—C	104.3	
$Ph_2Sn[Mn(CO)_5]_2$	Sn—Mn	2.70	2.78	Mn—Sn—Mn	117.0	26
				C—Sn—C	101.5	
$ClSn[Mn(CO)_5]_3$	Sn—Mn	2.737	2.78	Mn—Sn—Mn	116.5	32, 33
				Mn—Sn—Cl	101.5	
$Ph_2Sn\langle^{Mn(CO)_5}_{Co(CO)_4}$	Sn—Mn	2.73	2.78	Mn—Sn—Co	114.0	34–36
	Sn—Co	2.66	2.65	C—Sn—C	107.5	
$Ph_3SnRe(CO)_5$	Sn—Re	2.74	2.78			54
$Ph_3SnFe(CO)_2Cp$	Sn—Fe	2.536	2.67	Fe—Sn—C	113.4	42
				C—Sn—C	105.2	
$Me_2Sn[Fe(CO)_2Cp]_2$	Sn—Fe	2.64	2.67	Fe—Sn—Fe	124.0	39, 40
				C—Sn—C	96.0	
$(ONO)_2Sn[Fe(CO)_2Cp]_2$	Sn—Fe	2.56	2.67	Fe—Sn—Fe	126.0	39, 40
				O—Sn—O	67.4	
$Cl_2Sn[Fe(CO)_2Cp]_2$	Sn—Fe	2.43	2.67	Fe—Sn—Fe	128.6	41
				Cl—Sn—Cl	94.1	
$ClSn\langle^{Mo(CO)_3Cp}_{[Fe(CO)_2Cp]_2}$	Sn—Mo	2.89	2.77	Fe—Sn—Mo	116.9	43
	Sn—Fe	2.59	2.67	Fe—Sn—Fe	115.6	
				Fe—Sn—Cl	102.3	44
$Me_4Sn_3[Fe(CO)_4]_4$	Sn—Fe	2.62	2.67	Sn—Fe—Sn	77.9	
	Sn—Fe	2.75	2.67	Fe—Sn—Fe	98.0	
				Fe—Sn—Fe	116.0	
$n[Fe(CO)_4]_4$	Sn—Fe	2.54	2.67	Fe—Sn—Fe	68.9	45, 46
				Fe—Sn—Fe	133.0	
$Ph_3PbMo(CO)_3Cp$	Pb—Mo	2.90	3.11			54
$Ph_3PbRe(CO)_5$	Pb—Re	2.77	3.12			54
$Me_2Pb[Fe(CO)_2Cp]_2$	Pb—Fe	2.71	2.72	Fe—Pb—Fe	123.8	55
				C—Pb—C	102.0	

*Cp = π-cyclopentadienyl.

This effect agrees with the tendency to an increase in the *s*-character of the hybridised orbitals of the tin atom participating in the Sn–Fe bond (Bent's rule [37,38]). The changes examined can be explained on the basis of hypotheses concerning the existence of d_π–d_π-interaction between the completed $3d_\pi$ orbitals of iron and the vacant $5d_\pi$ orbitals of the tin atom, which is intensified when the π-acceptor ability of the SnX_2 group increases as a result of an increase in the electronegativity of substituent X. As will be shown subsequently, this explanation agrees well with the spectroscopic results and chemical properties of the organopolymetallic derivatives of metal carbonyls.

There is special interest in another class of derivatives of iron carbonyl containing the $Fe(CO)_4$ group. The iron atom in this group is capable of forming two covalent bonds with the atoms of Group IVB elements. On the basis of a measurement of molecular weights [49] and investigations of

infrared spectra[50,51] structures (I)–(IV) (Fig. 6) are proposed for several such clusters. Structures (III) and (IV) were confirmed by X-ray diffraction for the molecules $Me_4Sn_3[Fe(CO)_4]_4$ [44] and $Sn[Fe(CO)_4]_4$ [45,46] respectively.

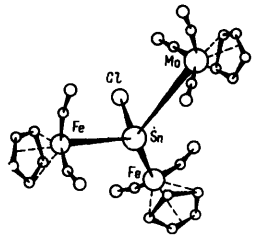


Figure 5. Geometry of the $ClSn[Fe(CO)_2Cp]_2$. $[Mo(CO)_3Cp]$ molecule.

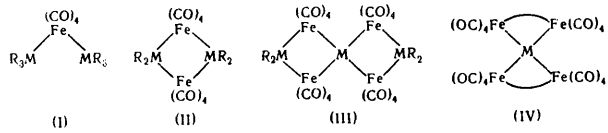


Figure 6. Structure of derivatives of iron tetracarbonyl containing an Fe–M bond where M = Ge, Sn, or Pb.

Table 2 gives the principal structural parameters of the compounds which contain a metal–metal bond between a transition metal atom and a Group IVB atom.

III. METHODS OF FORMATION OF COVALENT BONDS BETWEEN ATOMS OF TRANSITION METALS AND ELEMENTS OF GROUP IVB

This chapter considers the methods of preparation of compounds containing from one to four metal carbonyl groups bound to an atom of a Group IVB element. Such reactions of these compounds will be discussed in the following chapter.

Method I. Replacement of Halogen Atoms in Compounds of the $R_{4-n}MHal_n$ Type by Metal Carbonyl Groups

The most general method for the formation of metal–metal bonds is reaction between halogen derivatives of the Group IVB elements and the sodium derivatives of metal carbonyls. This method was first used (in a more general form) by Hein and coworkers[56–59] for the formation of a Pb–Fe bond in the reaction of R_3PbBr or R_3PbOH with $CaFe(CO)_4$.

Exchange reactions have been used to obtain most of the known organopolymetallic derivatives of the carbonyls of chromium, molybdenum, and tungsten[60–62], manganese[22,32,33,62–70], rhenium[62,66,67,71,72], iron[10,22,63,73–75], and cobalt[62,70,76–81]. Depending on the nature and ratio of the reagents and on the reaction conditions there is partial or complete replacement of halogen atoms by metal carbonyl groups:

$$R_{4-n}MX_n + nNaM'(CO)_xL \xrightarrow{THF} R_{4-n}M[M'(CO)_xL]_n + n\,NaX$$

$$R_{4-n}MX_n + m\,NaM'(CO)_xL \xrightarrow{THF} R_{4-n}X_{n-m}M[M'(CO)_xL]_m + m\,NaX$$

where M = Si, Ge, Sn, Pb; $M'(CO)_XL$ = $Cr(CO)_3Cp$, $Mo(CO)_3Cp$, $W(CO)_3Cp$, $Mn(CO)_5$, $Re(CO)_5$, $Fe(CO)_2Cp$, $Co(CO)_4$; R = H, alkyl, aryl; X = Cl, Br, I; n = 1–4; and m = 1–3.

The complexes which contain the $Fe(CO)_4$ group and have structures (I) and (II) (see Fig. 6) are obtained[50,82–84] by the following reactions:

$$2R_3MCl + Na_2Fe(CO)_4 \rightarrow (R_3M)_2Fe(CO)_4 + 2NaCl$$

$$2R_2MCl_2 + 2Na_2Fe(CO)_4 \rightarrow [R_2MFe(CO)_4]_2 + 4NaCl$$

where M = Ge, Sn, Pb; R = Me, Et, n-Bu, similar to the method used earlier by Hein.

Compounds with Sn–Ir bonds were synthesised with the aid of exchange reactions[85]:

$$R_{4-n}SnCl_n + n\,Na[Ir(CO)_3PPh_3] \rightarrow R_{4-n}Sn[Ir(CO)_3PPh_3]_n + n\,NaCl$$

where R = Me or Ph, and n = 1 or 2, as were compounds with Sn–Rh bonds[85]:

$$Me_3SnCl + Na[Rh(CO)_2(PPh_3)_2] \rightarrow Me_3SnRh(CO)_2(PPh_3)_2I + NaCl\ .$$

When the sodium derivatives of metal carbonyls react with polyhalide compounds of Group IVB elements mixtures of products with different degrees of substitution[64,65] are often formed, for example:

$$GeCl_4 + NaMn(CO)_5 \rightarrow Cl_3GeMn(CO)_5 + Cl_2Ge[Mn(CO)_5]_2 + [(OC)_5MnGeCl_2]\ .$$

By starting from halogen-containing organopolymetallic compounds, derivatives with a greater number of M–M' bonds can be obtained, including those with different metal carbonyl groups[86,87]:

$$R_2ClSnMn(CO)_5 + NaM'(CO)_xL \rightarrow R_2Sn[Mn(CO)_5][M'(CO)_xL] + NaCl$$

where $M'(CO)_XL$ = $Mo(CO)_3Cp$, $W(CO)_3Cp$, $Re(CO)_5$, or $Co(CO)_4$; R = Me or Ph.

By the replacement of the chlorine atoms in $Cl_2Sn[Fe(CO)_2Cp]_2$ by metal carbonyl groups clusters containing three different metals were obtained:

$ClSn[Mo(CO)_3Cp][Fe(CO)_2Cp]_2$[43,88], $Sn[Mo(CO)_3Cp]_2[Fe(CO)_2Cp]_2$[88], $ClSn[Mn(CO)_5][Fe(CO)_2Cp]_2$[73] and $ClSn[Re(CO)_5][Fe(CO)_2Cp]_2$[73].

Steric factors have a considerable effect on the nature of the products formed in reactions of this type. For example, compounds with four $M'(CO)_5$ groups (M' = Mn or Re) at germanium or tin atoms could not be obtained since distannanes are formed instead of the expected products[62,71]:

$$X_{4-n}Sn[M'(CO)_5]_n + NaM'(CO)_5 \rightarrow \begin{matrix}(OC)_5M' & & & & M'(CO)_5\\ & \diagdown & & \diagup & \\ (OC)_5M' & - & Sn & - & M'(CO)_5\\ & \diagup & & \diagdown & \\ (OC)_5M' & & & & M'(CO)_5\end{matrix}$$

where n = 1 or 3; M' = Mn or Re; X = Cl or Br. This is evidently explained by the large volume of the metal pentacarbonyl groups. Whereas many tin derivatives of the $XSn[M'(CO)_5]_3$ type have been obtained, where M' = Mn or Re and X = Me, Ph, Cl, Br, I, etc.[32,33,62,66], only one analogous germanium compound is known, $ClGe[Mn(CO)_5]_3$.[65] Instead of the corresponding bromo- and phenyl derivatives digermanes were obtained, for example:

$$2PhBr_2GeMn(CO)_5 + 4NaMn(CO)_5 \rightarrow \begin{matrix}(OC)_5Mn & & & & Mn(CO)_5\\ & \diagdown & & \diagup & \\ & & Ph-Ge-Ge-Ph & & \\ & \diagup & & \diagdown & \\ (OC)_5Mn & & & & Mn(CO)_5\end{matrix}\ .$$

The existence of the compounds $Sn[Fe(CO)_2Cp]_4$ [73] and $Sn[Mo(CO)_3Cp]_2.[Fe(CO)_2Cp]_2$ [88] shows that the steric hindrance produced by the $Mo(CO)_3Cp$ and $Fe(CO)_2Cp$ groups is much less than that due to the steric effects of the $Mn(CO)_5$ and $Re(CO)_5$ groups.

This type of method for the formation of M–M′ bonds includes the reaction of the halogen derivatives of Group IVB elements with the $[Co(CO)_4]^-$ anion [80,81] formed during the dissolution of cobalt carbonyl in nucleophilic solvents [89]:

$$3Co_2(CO)_8 + 12CH_3OH \rightarrow 2[Co(CH_3OH)_6]^{2+}[Co(CO)_4]_2^- + 8CO$$

$$R_{4-n}MCl_n + m[Co(CO)_4]^- \xrightarrow{CH_3OH} R_{4-n}Cl_{n-m}M[Co(CO)_4]_m$$

where M = Ge, Sn, or Pb; R = Me, n-Bu, or Ph; n = 1–3; m = 1–3.

Method 2. The Insertion of Ge^{II} and Sn^{II} Halides at Metal–Metal, Metal–Carbon, and Metal–Halogen Bonds

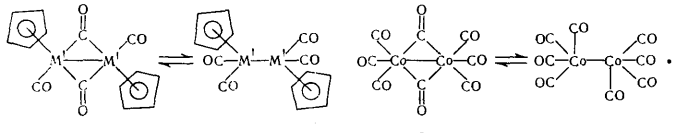
Several compounds which contain a bond between a Group IVB element and iron [24,74,90], cobalt [90–92], nickel [90], or ruthenium [93] atoms have been obtained as a result of the reaction of germanium(II) or tin(II) halides with dimeric carbonyls of the corresponding metals:

$$MX_2 + [M'(CO)_xL]_2 \rightarrow L(OC)_xM'–MX_2–M'(CO)_xL$$

where $M'(CO)_XL$ = $Fe(CO)_2Cp$, $Co(CO)_4$, $Co(CO)_3PR_3$, $Ni(CO)Cp$, $Ru(CO)_2Cp$; M = Ge or Sn; and X = Cl, Br, or I.

Reactions of this type are undergone both by the dihydrates of bivalent metal halides and by the anhydrous MX_2 in solutions in methanol, acetone, benzene or tetrahydrofuran (THF).

The reaction for the insertion of the MX_2 "carbenoids" at metal–metal bonds in dimeric carbonyls is based on the ability of Ge^{II} and Sn^{II} atoms to increase their covalency to four. As the experimental results show, this reaction is quite specific. They proceed comparatively readily with compounds which contain Fe–Fe, Co–Co, Ni–Ni, or Ru–Ru bonds, in the molecules of which in the crystalline state the metal–metal bonds are "maintained" by bridging carbonyl groups [94–96]. However, as the infrared spectra showed, in solutions the bridging forms $[M'(CO)_2Cp]_2$ (where M′ = Fe [97] or Ru [98]) and $Co_2(CO)_8$ [99–102] are in equilibrium with isomeric forms which do not contain bridging CO groups:



A rise in temperature shifts the equilibrium to the right.

The decrease in the coordination number of the metal atoms on going from the bridging form to the non-bridging form facilitates the approach of the MX_2 "carbenoids" to the M′–M′ bonds, which facilitates the insertion. In addition, the dissociation of $[Fe(CO)_2Cp]_2$ into $[Cp(CO)_2Fe]^{\cdot}$ radicals can be assumed to take place in nucleophilic solvents [103], and with $Co_2(CO)_8$ it is found that both $[(CO)_4Co]^{\cdot}$ radicals [104] and $[Co(CO)_4]^-$ anions [89,105] can be formed.

The insertion of $SnCl_2$ into phosphine derivatives of cobalt carbonyl free from bridging carbonyl groups has been effected [90–92]:

$$SnCl_2 + [Co(CO)_3PR_3]_2 \rightarrow Cl_2Sn[Co(CO)_3PR_3]_2$$

where R = n-Bu, Ph, or PhO. These reactions require more severe conditions and a much longer time than for $Co_2(CO)_8$. The insertion is hindered by increase in the π-acceptor capability of the ligands in the order: Bu_3P < < Ph_3P < $(PhO)_3P$.

Until recently insertions at metal–metal bonds in dinuclear carbonyls of molybdenum, tungsten, manganese, and rhenium, the fragments of which are bonded either in the crystalline state [6,7,9] or in solutions (according to the infrared spectra [106,107]) solely by an M′–M′ bond had not been effected. The reaction of $[Mo(CO)_3Cp]_2$ with $SnCl_2$ leads to the formation of $Cl_3SnMo(CO)_3Cp$. [24] The dimeric derivative of manganese carbonyl containing the 1,2-bis-diphenylphosphinoethane ligand reacts with $SnCl_2$ but the insertion product is again not obtained [108]:

$$[Mn(CO)_3L]_2 + SnX_2 \xrightarrow{\text{Acetone}} X_3SnMn(CO)_xL_y$$

where L = $Ph_2PCH_2CH_2PPh_2$; X = Cl, Br; x = 3 for y = 1; x = 1 for y = 2.

Manganese and rhenium carbonyls do not react with MX_2, [24,108] even on boiling in THF for three weeks [90]. It was recently observed [109] that to introduce MX_2 "carbenoids" at Mn–Mn and Re–Re bonds either elevated temperature or ultraviolet radiation, leading to the homolytic fission of these bonds, is necessary.

Hence the possibility of effecting insertion at M′–M′ bonds is determined by the stability of these bonds under the reaction conditions.

The insertion of "carbenoid" systems at transition metal–carbon bonds was first achieved at C–Fe bonds [110]:

$$MeFe(CO)_2Cp + GeCl_2\cdot C_4H_8O_2 \xrightarrow{\text{(dioxan)}} MeCl_2GeFe(CO)_2Cp$$

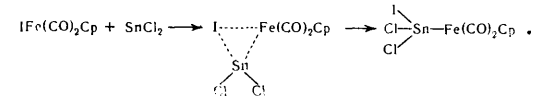
whereas with the C–W bond reaction with $SnCl_2$ led to the replacement of a methyl group by $SnCl_3$: [24]

$$MeW(CO)_3Cp + SnCl_2 \xrightarrow{\text{(acetone)}} Cl_3SnW(CO)_3Cp\ .$$

The reactions of halogen derivatives of metal carbonyls with germanium(II) and tin(II) halides were studied. $SnCl_2$ reacts with $ClFe(CO)_2Cp$ in methanol as follows [24]:

$$ClFe(CO)_2Cp + SnCl_2\cdot 2H_2O \rightarrow Cl_3SnFe(CO)_2Cp\ .$$

The reaction may proceed either by the insertion of $SnCl_2$ at the Fe–Cl bond or by the replacement of a chlorine atom in $ClFe(CO)_2Cp$ by $[SnCl_3]^-$ by an S_N1 or S_N2 mechanism. To find the mechanism $IFe(CO)_2Cp$ was treated with a tenfold excess of $SnCl_2$ as a result of which the complex $CH_3OH.ICl_2SnFe(CO)_2Cp$ was obtained [111]. Evidently the insertion of a "carbenoid" really does occur here, possibly proceeding with preliminary coordination of Cl_2Sn to the iron and iodine atoms and subsequent intramolecular migration of the iodine atom:



The complex of $GeCl_2$ with dioxan reacts smoothly with $ClFe(CO)_2Cp$ with the formation of $Cl_3GeFe(CO)_2Cp$. [112] In the reaction of this same complex with $IFe(CO)_2Cp$ a mixture of products is formed, in which $Cl_3GeFe(CO)_2Cp$ and $I_3GeFe(CO)_2Cp$ are present, as a comparison of the chemical shifts of the protons of the cyclopentadienyl ring shows. This can be due to the ready disproportionation of the compound expected:

$$5\ ICl_2GeFe(CO)_2Cp \rightarrow 3\ Cl_3GeFe(CO)_2Cp + I_2ClGeFe(CO)_2Cp + I_3GeFe(CO)_2Cp\ .$$

By analogy with the reactions of $GeCl_2$ and $MeFe(CO)_2Cp$ [110] it can be assumed that the reaction between the MX_2 halides and compounds with Fe–Hal bonds also proceeds by the insertion mechanism.

Method 3. Reaction of Trichlorogermane with Halogen Derivatives of Metal Carbonyls

The possibility of the formation of metal–metal bonds by reactions of this type was first demonstrated by the condensation of trichlorogermane with pentacarbonylmanganese chloride [113]:

$$Cl_3GeH + ClMn(CO)_5 \xrightarrow{(THF)} Cl_3GeMn(CO)_5 + HCl \ .$$

The compounds $Cl_3GeMo(CO)_3Cp$, $Cl_3GeW(CO)_3Cp$, [114] and $Cl_3GeFe(CO)_2Cp$ [115] were obtained by the same method. Reactions of this type take place in THF solutions or in ether–dioxan mixtures.

It is known [116] that in $HGeCl_3$ there is an equilibrium between the bivalent and quadrivalent forms of germanium, and the presence of ethers facilitates the protonic dissociation of the germyl hydrogen:

$$HGeCl_3 \rightleftarrows H^+ + GeCl_3^- \rightleftarrows H^+ + Cl^- + GeCl_2$$

and the formation of ether addition compounds of the type $[R_2O \rightarrow H \leftarrow OR_2]^+GeCl_3^-$. In dioxan the dissociation goes even further and the complex $Cl_2Ge.C_4H_8O_2$ is formed. As shown above, this complex reacts with $ClFe(CO)_2Cp$, most probably by insertion at the Fe–Cl bond. In the reaction of $HGeCl_3$ with $[Fe(CO)_2Cp]_2$ in THF, $Cl_3Ge[Fe(CO)_2Cp]_3$ formed in additon to $Cl_3GeFe(CO)_2Cp$. [115]

It can be assumed that the reaction of metal halogenocarbonyls with $HGeCl_3$ proceeds either by the insertion of $GeCl_2$ at the M′–Cl bond or by an ionic mechanism with participation of the $GeCl_3^-$ anion by analogy with the reactions of alkyl halides with trichlorogermane leading to compounds of the $RGeCl_3$ type [116]. Possibly both these mechanisms compete but they have not yet been distinguished.

Method 4. Replacement of the Mercury Atom in Mercury Derivatives of Metal Carbonyls by Tin(II) Halides

Sn–M′ bonds are formed in the reaction of SnX_2 with $XHgM'(CO)_xL$ or $Hg[M'(CO)_xL]_2$ in acetone or ethyl acetate [91,117]:

$$RHgR' + SnX_2 \rightarrow X_2SnRR' + Hg \quad (1)$$
$$RHgX + SnX_2 \rightarrow X_2SnR + Hg \quad (2)$$

where R and R′ = $Mo(CO)_3Cp$, $W(CO)_3Cp$, $Fe(CO)_2Cp$, $Co(CO)_4$, $Co(CO)_3PBu_3$; X = Cl or Br. The initial stage of reaction (1) may be the introduction of "carbenoid" groups: $R–Hg–R–SnX_2 \rightarrow [R–Hg–SnX_2–R]$. The intermediate compound is unstable owing to the low strength of the Hg–Sn bond and readily decomposes:

$$[R—Hg—SnX_2—R] \rightarrow Hg + X_2SnR_2.$$

Reaction (2) evidently proceeds by another mechanism. Unlike the electrophilic insertion of SnX_2 mentioned above here nucleophilic attack by SnX_3^- formed in the solution on the RHg^+ or $RHg[(Solv)]^+$ cation is possible:

$$R—Hg—X + SnX_3^- \xrightarrow{(Solv)} [RHgSnX_3] \rightarrow X_2SnR + Hg \ .$$

Method 5. Reaction of Silanes with Dimers of Metal Carbonyls

In the reaction of silanes with cobalt carbonyl a compound with a Si–Co bond is formed readily [118]. The reaction of silanes with dinuclear metal carbonyls serves as a preparative method for the synthesis of various silyl derivatives of molybdenum [119], manganese and rhenium [67, 70, 119], iron [119], cobalt [50, 70, 120, 121], and nickel [119]:

$$2R_3SiH + [M'(CO)_xL]_2 \rightarrow 2R_3SiM'(CO)_xL + H_2$$

where $M'(CO)_xL$ = $Mo(CO)_3Cp$, $Mn(CO)_5$, $Re(CO)_5$, $Fe(CO)_2Cp$, $Co(CO)_4$, $Ni(CO)Cp$; R = H, alkyl, aryl, halogen. It should be noted that the reaction with cobalt carbonyl is very fast even at room temperature, whereas very severe conditions are necessary with manganese and rhenium carbonyls.

Probably the initial stage in these reactions is the formation of $HM'(CO)_xL$, which then reacts with the silane:

$$R_3SiH + HM'(CO)_xL \rightarrow R_3SiM'(CO)_xL + H_2 \ .$$

Confirmation of this mechanism is given by the quantitative formation of compounds of the type $R_3SiCo(CO)_4$ in the reaction of silanes with either cobalt carbonyl or $HCo(CO)_4$. [121]

The reaction of $HSiCl_3$ with $Fe_3(CO)_{12}$ gives a compound with two terminal Cl_3Si groups at the iron atom, $(Cl_3Si)_2Fe(CO)_4$, and in reaction with $Fe(CO)_5$ in addition to this compound the cluster $[Cl_2SiFe(CO)_4]_2$ with two bridging silicon atoms is obtained [119].

Evidently the reaction of alkylgermanes [50,120] and alkylstannanes [51] with metal carbonyls can be classified among this type of reaction:

$$Et_3GeH + Co_2(CO)_8 \rightarrow Et_3GeCo(CO)_4$$
$$2Me_3SnH + Fe(CO)_5 \rightarrow (Me_3Sn)_2Fe(CO)_4 + H_2 + CO$$
$$2Me_2SnH_2 + 2Fe(CO)_5 \rightarrow [Me_2SnFe(CO)_4]_2 + 2H_2 + 2CO \ .$$

Apart from the general methods for the formation of M–M′ bonds considered above, there are specific methods applicable for the synthesis of individual organopolymetallic derivatives of metal carbonyls.

Compounds with Si–Mo or Si–W bonds were obtained by the reaction [122]:

$$HM'(CO)_3Cp + Me_2SiNMe_2 \xrightarrow{(THF)} Me_2SiM'(CO)_3Cp + Me_2NH.$$

Metal–metal bonds are formed by the photolytic reaction [123]:

$$Ph_4AsMCl_3 + M'(CO)_6 \xrightarrow{(CH_2Cl_2)} Cl_3MM'(CO)_5AsPh_4 + CO$$

where M = Ge or Sn; M′ = Cr, Mo, W.

Compounds of the $Cl_3MFe(CO)_4AsPh_4$ type were obtained [123] by a similar method from $Fe(CO)_5$. The formation of products with two metal–metal bonds of the $(Cl_3M)_2M'(CO)_4(AsPh_4)_2$ type, where M = Ge or Sn and M′ = Cr, Mo, or W, is also possible.

Compounds with M–M′ bonds were obtained [124] by reactions with oxidative eliminations, for example:

$$(bipy)Mo(CO)_4 + MeSnCl_3 \rightarrow MeCl_2SnMoCl(CO)_3(bipy) + CO \ .$$

The formation of a Ge–Mn bond was possible as a result of the reaction:

$$GeH_4 + 2HMn(CO)_5 \xrightarrow{(THF)} H_3Ge[Mn(CO)_5]_3 + 2H_2 \ .$$

In this even traces of $H_3GeMn(CO)_5$ or $HGe[Mn(CO)_5]_3$ were not observed although they might have been formed by the simple replacement of hydrogen atoms in the germane by the $Mn(CO)_5$ group. It is assumed that this reaction proceeds by the reduction of GeH_4 by the manganese carbonyl to GeH_2, which then adds two $Mn(CO)_5$ radicals. Traces of $H_2Ge[Mn(CO)_5]_2$ were observed in the reaction of GeH_4 with $Mn_2(CO)_{10}$. However, neither GeH_4 nor H_3GeK react with $ClMn(CO)_5$ or $BrMn(CO)_5$. [125].

Most of the compounds which contain the $Fe(CO)_4$ group were obtained as a result of specific reactions. Thus, compounds of the type $R_nSnR'_{4-n}$, where R = alkyl and R′ = vinyl or phenyl, react with $Fe(CO)_5$ to form clusters

of the $[R_2SnFe(CO)_4]_2$ type [49]. It is characteristic that these reactions are possible only for such compounds in which organic groups bound to the tin atom through sp^3 and sp^2 hybridised carbon atoms are present, for example, Me_2SnPh_2 or $Bu_2Sn(CH=CH_2)_2$; the groups bound to tin by the sp^2 carbon atom are more readily detached. Evidently the initial stage of the reaction is the formation of an unstable π-complex with participation of an iron atom.

The reaction

$$Bu_3SnCl + Fe(CO)_5 \rightarrow [Bu_2SnFe(CO)_4]_2 + Bu_4Sn_2[Fe(CO)_4]_4 + Sn[Fe(CO)_4]_4$$

was studied in detail [46,51]. It was suggested that initially a compound with structure (I) (Fig. 6) is formed:

$$2Bu_3SnCl + Fe(CO)_5 \rightarrow (Bu_3Sn)_2Fe(CO)_4 + CO,$$

which then disproportionates:

$$2(Bu_3Sn)_2Fe(CO)_4 \rightarrow [Bu_3SnFe(CO)_4]_2 + 2Bu_4Sn\ .$$

The composition of the mixture of products depends greatly on the reaction conditions. Thus after intensive boiling for 70 h only $Sn[Fe(CO)_4]_4$ is isolated. This compound can also be obtained by other methods:

$$Bu_6Sn_2 + Fe(CO)_5 \rightarrow Sn[Fe(CO)_4]_4 \leftarrow SnCl_2 + Fe(CO)_5\ .$$

Compounds having structure (II) (Fig. 6) are also formed by the reaction [126,127]:

$$R_2Sn(C{\equiv}CR')_2 + Fe_3(CO)_{12} \rightarrow [R_2SnFe(CO)_4]_2\ .$$

Oxidative elimination leads to compounds with structure (I), for example [124]:

$$SnX_4 + Fe(CO)_5 \rightarrow X_3SnFeX(CO)_4 \rightarrow (X_3Sn)_2Fe(CO)_4.$$

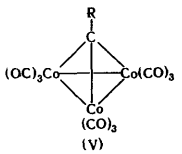
A series of specific methods for the formation of M–Co bonds are known. The direct reaction of MX_4 with cobalt carbonyl [77-81] can give halogen derivatives with from one to three $Co(CO)_4$ groups:

$$GeCl_4 + Co_2(CO)_8 \rightarrow Cl_{4-n}Ge[Co(CO)_4]_n + CoCl_2 + CO$$
$$4SnX_4 + 9Co_2(CO)_8 \rightarrow 4XSn[Co(CO)_4]_3 + 2CoX_2 + 24CO$$

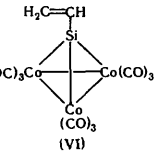
where X = Cl, Br, or I and n = 1 or 2. It is thought that in these reactions after the Co–Co bond is broken unstable carbonylcobalt halides are formed, which then decompose. The rate of these reactions decreases considerably with drop in the nucleophilic nature of the solvent in the series: THF > benzene > heptane [77]. It is not ruled out that reaction in THF is greatly facilitated by the reaction of $Co_2(CO)_8$ with the solvent, leading to the formation of the $[Co(CO)_4]^-$ anion. Clusters with an $RSnCo_3$ skeleton were obtained [79,80,102] by a similar method:

$$RSnCl_3 + Co_2(CO)_8 \rightarrow RSn[Co(CO)_4]_3 \text{ (where R=Me, Bu)}\ .$$

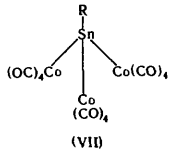
Compounds of the type $RC[Co(CO)_3]_3$ with structure (V) are formed [128,129] in the reaction of organic trihalogenoderivatives with $Co_2(CO)_8$:



(V)



(VI)



(VII)

Kettle and Khan [130] obtained a compound with Si–Co bonds for which the structure (VI) is proposed:

$$(CH_2{=}CH)_4Si + Co_2(CO)_8 \rightarrow CH_2{=}CHSi[Co(CO)_3]_3\ .$$

Tris(tetracarbonylcobalt) derivatives of tin (VII) do not contain Co–Co bonds, unlike the tris(tricarbonylcobalt) derivatives of carbon and silicon (V) and (VI) formed in similar reactions. It is interesting that the products of the reaction of tetravinylstannane with $Co_2(CO)_8$ differ depending upon the solvent: $(CH_2{=}CH)_2Sn[Co(CO)_4]_2$ is formed in pentane whereas in THF $MeC[Co(CO)_3]_3$ is formed. The formation of the latter is evidently explained by the conversion of the vinyl group into an ethylidene group during the reaction. The reasons for the difference in the structure of the complexes with an $RMCo_3$ skeleton, where M = C, Si, or Sn are still unexplained.

When tin(II) acetate reacts with $Co_2(CO)_8$ a mixture of $(CH_3CO_2)_2Sn[Co(CO)_4]_2$ and $CH_3CO_2Sn[Co(CO)_4]_3$ is formed [131].

As a result of the reaction of bis-(2,4-pentadionato)$SnCl_2$ with $[Co(CO)_4]^-$ compounds with a 6-coordinated tin atom are obtained [132]:

$$(C_5H_7O_2)_2SnCo_2(CO)_7,\quad (C_5H_7O_2)_2Sn[Co(CO)_4]_2 \text{ and } (C_5H_7O_2)_2ClSnCo(CO)_4.$$

IV. PROPERTIES OF ORGANOPOLYMETALLIC COMPOUNDS

Derivatives of Group IVB elements and metal carbonyls which contain metal–metal bonds are usually crystalline substances soluble in the usual organic solvents and insoluble in water. These compounds decompose comparatively readily in solution. In the solid state they are rather stable to the action of heat, light, oxygen, and atmospheric moisture. The stability of the compounds which differ in the transition metal atom increases considerably with increase in the atomic number of the metal within each group, for example, in the series Cr < Mo < W. With increase in the number of metal carbonyl groups the stability of the compounds falls slightly. In the series of compounds which differ only in the atoms of the Group IVB elements the stability of the lead derivatives is much less than that of its group analogues. Usually, with increase in the electronegativity of the substituent at the non-transition element the stability of the compounds increases.

The following reaction modes are characteristic for the compounds of the $X_{4-n}M[M'(CO)_xL]_n$ type: (1) substitution of M for X at the Group IVB element; (2) reactions at the M–M' bonds, and (3) replacement of the carbonyl groups at the transition metal atoms by other ligands. Furthermore, some of these compounds are capable of forming addition products with electron-donating reagents.

1. Replacements at the Group IVB Element

It is known [133,134] that halogenogermanes and halogenostannanes with organic groups readily exchange halogen atoms for other substituents. Halogen derivatives of germanium and tin containing metal carbonyl groups are also capable of exchanging halogen atoms for other atoms or groups whilst retaining the metal–metal bonds. Thus the chlorine atoms in $Cl_3GeFe(CO)_2Cp$ are replaced by acetoxy-groups [112]:

$$Cl_3GeFe(CO)_2Cp + 3CH_3COOK \rightarrow (CH_3COO)_3GeFe(CO)_2Cp + 3KCl\ .$$

Compounds are obtained with different functional groups at the germanium or tin atoms bound to two metal carbonyl groups:

$$Cl_2M[M'(CO)_xL]_2 + 2Y^- \rightarrow Y_2M[M'(CO)_xL]_2 + 2Cl^-\ ,$$

where $M'(CO)_xL$ = Mo $(CO)_3Cp$, W $(CO)_3Cp$; M=Sn[135], Mn $(CO)_5$; M=Ge[136]; Fe $(CO)_2Cp$, M = Ge, Sn[79,137]; Y=CH_3COO, MeO, EtS, SCN, OH, S, ONO, NO_3.

In the reaction with organic derivatives of lithium, sodium, or magnesium replacement of halogen atoms by organic groups occurs[73,74,135,137,138], for example:

$$I_2Ge[Fe(CO)_2Cp]_2 + 2MeLi \rightarrow Me_2Ge[Fe(CO)_2Cp]_2 + 2LiI$$

$$Cl_2Sn[Mo(CO)_3Cp]_2 + 2C_5H_5Na \rightarrow (C_5H_5)_2Sn[Mo(CO)_3Cp]_2 + 2NaCl$$

$$Br_3GeMn(CO)_5 + 3PhMgBr \rightarrow Ph_3GeMn(CO)_5 + 3MgBr_2 .$$

On passing gaseous HBr through solutions of $Cl_3GeMn(CO)_5$ or $Cl_2Ge[Mn(CO)_5]_2$ chlorine atoms are quantitatively replaced by bromine[138].

It was noted above that in the reaction of compounds of Group IVB elements containing several halogen atoms with the sodium derivatives of metal carbonyl mixtures of products with different degrees of substitution are obtained. A convenient method for the synthesis of individual halogen-containing compounds is the exchange of acetoxy-groups for halogen atoms:

$$(CH_3COO)_nGe[M'(CO)_xL]_{4-n} + n\,HX \rightarrow X_nGe[M'(CO)_xL]_{4-n} + n\,CH_3COOH$$

where $M'(CO)_xL = Mn(CO)_5$,[136] $Fe(CO)_2Cp$,[112,137] X = F, Cl, Br, I; $n = 2$ or 3.

Compounds with Ge–Fe bonds have been reduced[74]:

$$Cl_2Ge[Fe(CO)_2Cp]_2 + 2NaBH_4 \rightarrow H_2Ge[Fe(CO)_2Cp]_2$$

but attempts to obtain similar compounds with M–Mn or M–Re bonds were unsuccessful since reaction with $LiAlH_4$ or $NaBH_4$ is accompanied by the breaking of M–M′ bonds. Alkylation of compounds with Sn–Mo or Sn–W bonds could not be brought about with Grignard reagents[135]. These facts show the decrease in the stability of the M–M′ bonds under the conditions of these reactions is in the order M–Fe > M–Re ≃ M–Mn > M–W ≃ M–Mo, where M = Ge or Sn.

Carbonyl derivatives of the type $R_{4-n}M[M'(Cl)_xL]_n$, where R is an organic radical, react with halogens or hydrogen halides in two (sometimes competing) directions: either with partial or complete replacement of R or with breaking of the M–M′ bond. The direction of the reaction is determined primarily by the nature of the reactants and also by the quantitative ratio of the reagents and the reaction conditions.

$H_3SiMn(CO)_5$ was rather inert to the action of HCl;[69] gradual replacement of hydrogen atoms takes place only at 75°, and the Si–Mn bond is retained:

$$H_3SiMn(CO)_5 + n\,HCl \rightarrow H_{3-n}Cl_nSiMn(CO)_5 + n\,H_2$$

where $n = 1$–3. The considerable differences in the reactivity of the germanium and tin derivatives of the corresponding metal carbonyls is connected on the one hand with the lesser stability of the C–Sn bond in comparison with C–Ge. On the other hand an analysis of the reactions given below suggests that the stability of the Sn–M′ bonds is much greater than that of the Ge–M′ bonds. The triphenylgermyl derivatives of manganese and rhenium carbonyls do not react with HCl,[64,72] unlike the corresponding tin derivatives, which react with hydrogen halides with partial or complete replacement at the tin atom[22,71]. The Ph_3Sn derivatives of molybdenum, tungsten[60,135], iron[73], and cobalt[77] carbonyls behave similarly:

$$Ph_3SnM'(CO)_xL + n\,HX \rightarrow Ph_{3-n}X_nSnM'(CO)_xL + n\,C_6H_6$$

where X = Cl, Br, I and $n = 1$–3. Diphenylstannanes containing two metal carbonyl groups react with hydrogen halides, usually with retention of the Sn–M′ bonds[72,73,86,135]:

$$Ph_2Sn[M'(CO)_xL]_2 + 2\,HX \rightarrow X_2Sn[M'(CO)_xL]_2 + 2\,C_6H_6 .$$

It is characteristic that $Ph_2Sn[Mn(CO)_5][Co(CO)_4]$ reacts with HCl with replacement of only one phenyl group[86] but $Ph_2Sn[Co(CO)_4]_2$ does not undergo this reaction at all[77]. Evidently, the Sn–C bond is stabilised as a result of the addition of the electronegative $Co(CO)_4$ group to the tin atom. $Ph_2Ge[Re(CO)_5]_2$ reacts with HCl with the loss of one metal carbonyl group and not a phenyl group[72].

In the reaction of halogens with Ph_3Sn derivatives of manganese and rhenium carbonyls, depending on the ratio of the reagents mono-, di-, or tri-halogeno-derivatives are formed with retention of the Sn–M′ bonds[22,71,72]:

$$Ph_3SnM'(CO)_5 + n\,X_2 \rightarrow Ph_{3-n}X_nSnM'(CO)_5 + n\,PhX .$$

The action of halogens on $Ph_2Sn[Re(CO)_5]_2$ leads to the replacement of one of the two phenyl groups (depending on the ratio of the reagents)[71], whereas the analogous manganese compound reacts with the breaking of both C–Sn bonds and one Sn–Mn bond[22].

The reaction of $Ph_3GeMn(CO)_5$ and its rhenium analogue with chlorine or bromine at room temperature leads to breaking of the Ge–M′ bonds without replacement of the phenyl groups at the germanium atom. On the other hand, at temperatures above 70°, irrespective of the ratio of the reactants, all three phenyl groups are replaced by halogen atoms with retention of the Ge–M′ bond[64,72]:

$$Ph_3GeM'(CO)_5 + 3\,X_2 \rightarrow X_3GeM'(CO)_5 + 3\,PhX .$$

The direct action of halogens does not bring about replacement of three phenyl groups in Ph_4Ge or Ph_3GeX, or even one in Ph_2GeX_2, where X = Cl, Br, or I. The capability for ready and simultaneous replacement of three phenyl groups in $Ph_3GeM'(CO)_5$ shows the greater electron-donating ability of the $Mn(CO)_5$ and $Re(CO)_5$ groups in comparison with the phenyl groups.

The introduction of halogen atoms into phenylgermyl derivatives has been shown[65] to greatly strengthen Ge–Mn bond and to some extent the Ge–C bond, in comparison with the corresponding bonds in $Ph_3GeMn(CO)_5$. Thus at room temperature $Ph_2BrGeMn(CO)_5$ does not react with bromine, and at 72° one phenyl group is readily replaced by bromine, but $PhBr_2GeMn(CO)_5$ reacts very slowly with an excess of bromine at 72° to form $Br_3GeMn(CO)_5$.

Hence it can be taken as proved that the Ge–C bond in the germyl derivatives of the Group VII metal carbonyls is broken under the action of halogens much more readily than in ordinary organogermanium compounds.

Unlike the rearrangements[133]:

$$Ph_2GeX_2 + GeX_4 \rightarrow 2\,PhGeX_3$$

where X = Cl, Br, or I, which take place at high temperature in the presence of catalysts, the rearrangement of germanes which contain an $Mn(CO)_5$ group proceeds without a catalyst at a temperature not much above the melting point of the mixture of reagents[64]:

$$Ph_2BrGeMn(CO)_5 + Br_3GeMn(CO)_5 \rightarrow 2\,PhBr_2GeMn(CO)_5 .$$

Reactions with rearrangement at the tin atom are used[22] as a convenient method for making monohalogeno-derivatives:

$$PhBr_2SnMn(CO)_5 + Ph_3SnMn(CO)_5 \rightarrow 2\,Ph_2BrSnMn(CO)_5 .$$

The possibility of the rearrangement of atoms of different halogens in germyl derivatives of iron carbonyl has been demonstrated[112]:

$$Cl_3GeFe(CO)_2Cp + I_3GeFe(CO)_2Cp \rightarrow Cl_2IGeFe(CO)_2Cp + ClI_2GeFe(CO)_2Cp .$$

With derivatives of metal carbonyls which contain lead replacement at the lead atom is not observed although the

Pb–C bond is the weakest in the series of organometallic derivatives of the Group IVB elements [134]; the Pb–M′ bond is broken first.

2. Reaction of Compounds of the $X_{4-n}M[M'(CO)_xL]_n$ type at M–M′ Bonds

A. Breaking of the metal–metal bond. Unlike $H_3SiMn(CO)_5$ its addition product with pyridine reacts rapidly with HCl with quantitative breaking of the Si–Mn bond [69]:

$$H_3SiMn(CO)_5 \cdot 2C_5H_5N + 3HCl \rightarrow H_3SiCl + HMn(CO)_5 + 2C_5H_5N \cdot HCl .$$

$H_3SiCo(CO)_4$ is broken by HCl or water with the formation of cobalt carbonyl hydride [76]:

$$H_3SiCo(CO)_4 + HX \rightarrow H_3SiX + HCo(CO)_4$$

where X = Cl or OH. As noted above, the action of hydrogen halides does not break the M–M′ bond in germanium and tin derivatives of the $Ph_3MM'(CO)_xL$ type or in $Ph_2Sn[M'(CO)_xL]_2$, [22,60,64,72,73,77,135] but one of the Sn–Fe bonds in $PhSn[Fe(CO)_2Cp]_3$ is broken under the action of HCl:[73]

$$PhSn[Fe(CO)_2Cp]_3 + 3HCl \rightarrow Cl_2Sn[Fe(CO)_2Cp]_2 + ClFe(CO)_2Cp .$$

This shows that the M–M′ bond is weakened with increase in the number of metal carbonyl groups at the non-transition element atom. $Ph_2Sn[Mn(CO)_5][Co(CO)_4]$ reacts in a different manner with HCl and HBr: under the action of HCl only one phenyl group is replaced [86] whereas reaction with HBr under these conditions leads to the replacement of both phenyl groups and breaking of the Sn–Co bond [77]:

$$Ph_2Sn[Mn(CO)_5][Co(CO)_4] + HBr \rightarrow Br_2SnMn(CO)_5 .$$

Differences in the reactivity of metal–metal bonds in relation to the action of halogens are more noticeable. For example, in compounds of the $Ph_3MM'(CO)_5$ type (M′ = Mn or Re) the Sn–M′ bond is not broken by halogens at either room or elevated temperature. Whereas Ge–Mn or Ge–Re bonds are stable to the action of halogens at temperatures above 70° they are broken at room temperature [64,72]:

$$Ph_3GeM'(CO)_5 + X_2 \rightarrow Ph_3GeX + XM'(CO)_5 .$$

Probably the reaction of $Ph_3GeM'(CO)_5$ with halogens proceeds by different mechanisms at different temperatures in accordance with a change in the relative strength of the Ge–C and Ge–M′ bonds. Above 70° the rapid homolytic breaking of the Ge–C bond becomes possible [134] and at 20°C the Ge–Mn and Ge–Re bonds become less resistant to the action of halogens and are broken more rapidly than the Ge–C bonds, which are relatively more stable under these conditions. The breaking of Ge–M′ bonds at low temperature can proceed heterolytically, although the possibility of a homolytic process is not excluded.

Under the action of halogens the M–M′ bonds in $Ph_3SnFe(CO)_2Cp$, [22] $Ph_3MM'(CO)_3Cp$ (M = Sn or Pb), and $Ph_2Sn[M'(CO)_3Cp]_2$ (M′ = Cr, Mo, W) [135] are broken. Bromine detaches one metal carbonyl group from $Ph_2Ge[M'(CO)_5]_2$, where M′ = Mn or Re:[64,71,72]

$$Ph_2Ge[M'(CO)_5]_2 + Br_2 \rightarrow Ph_2BrGeM'(CO)_5 + BrM'(CO)_5 .$$

An excess of chlorine splits not only both the Sn–C bonds in $Ph_2Sn[Mn(CO)_5]_2$ but also one of the Sn–Mn bonds, $Cl_3SnMn(CO)_5$ being formed [22]. In the analogous rhenium compound both the Sn–Re bonds are retained under the action of chlorine [71], which shows that the Sn–Re bond is stronger than the Sn–Mn bond.

The bonds of transition metal atoms with lead are less stable. Reaction of $Ph_3PbMn(CO)_5$, $Et_2Pb[Mn(CO)_5]_2$, [22] and $Ph_3PbRe(CO)_5$ [60] with halogens and HCl leads to the complete decomposition of the molecule.

Apart from the breaking of the M–M′ bond under the action of halogens and hydrogen halides, some reactions of this type with other agents are known. The Si–Mn bond is readily broken by ammonia [69]:

$$2H_3SiMn(CO)_5 + NH_3 \rightarrow 2HMn(CO)_5 + (H_3Si)_2NH .$$

A similar reaction was observed for $H_3SiCo(CO)_4$ with the difference that here disilazane was decomposed to SiH_4, $(H_3Si)_3N$, and polymeric products, probably owing to the greater acidity of $HCo(CO)_4$ compared with that of $HMn(CO)_5$.

The reaction of $H_3SiCo(CO)_4$ with mercury(II) iodide is [76]:

$$2H_3SiCo(CO)_4 + HgI_2 \rightleftarrows 2H_3SiI + Hg[Co(CO)_4]_2$$

and the equilibrium is greatly displaced to the right.

Reactions with redistribution at the atoms of the non-transition elements which use the M–M′ bond are also known, for example [24]:

$$Cl_2Sn[Fe(CO)_2Cp]_2 + SnCl_4 \rightarrow 2Cl_3SnFe(CO)_2Cp$$

and also reactions with substitution at the cobalt atom, as a result of which the Si–Co bond is broken and a Ge–Co bond is formed [121]:

$$Me_3SiCo(CO)_4 + GeF_4 \rightarrow F_3GeCo(CO)_4 + Me_3SiF .$$

B. Insertion at Metal–Metal Bonds. In the reaction of perfluoroethylene with $Me_3SnMn(CO)_5$, $Me_3GeMn(CO)_5$, or $Me_3SnCo(CO)_4$ under ultraviolet radiation in pentane compounds containing M–C–C–M′ chains, where M = Ge or Sn and M′ = Mn or Co are obtained [139–142]. Whereas only one $CF_2{=}CF_2$ molecule is inserted per Sn–Mn bond, several perfluoroethylene molecules can be inserted at a Ge–Mn bond with formation of compounds of the $Me_3Ge(C_2F_4)_nMn(CO)_5$ type. As well as insertion products a mixture of fluorinated derivatives is formed in these reactions: Me_3MF, $C_5F_9Mn(CO)_5$, and other organofluorine derivatives of manganese carbonyls.

The reaction mechanism for the introduction of perfluoroethylene at M–M′ bonds has not been explained. Despite the fact that the reaction proceeds only under conditions favourable to free-radical processes, the products characteristic of reactions of Me_3M' radicals with perfluoroalkenes are not observed. The appearance in the reaction mixture of the fluoro-derivatives of germanium, of tin, and of manganese carbonyl can be explained by the decomposition of the insertion products as follows:

$$Me_3M{-}Mn(CO)_5 + CF_2{=}CF_2 \xrightarrow{h\nu} Me_3M{-}CF_2{-}CF_2{-}Mn(CO)_5$$

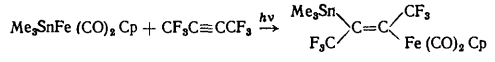
$$Me_3MCF_2CF_2Mn(CO)_5 \rightarrow CF_2{=}CF{-}Mn(CO)_5 + Me_3MF$$

$$CF_2{=}CF{-}Mn(CO)_5 \xrightarrow{-2CO} [CF_2{=}CFMn(CO)_4]_2 \qquad CF_2{=}CF{-}Mn(CO)_5 \xrightarrow{+CO} CF_2{=}CF{-}\overset{\overset{O}{\|}}{C}{-}Mn(CO)_5 .$$

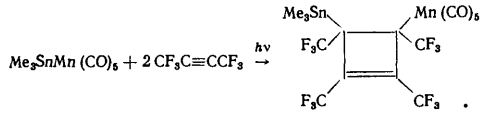
Evidently $Me_3GeC_2F_4Mn(CO)_5$ is more stable than the analogous tin compound.

Unlike perfluoroethylene, $CF_2{=}CFCl$ and $CF_2{=}CFH$ react with $Me_3MMn(CO)_5$ and $Me_3SnCo(CO)_4$ to form not insertion products but mixtures of different fluorinated organometallic compounds. Perfluoropropene also does not form an addition product with $Me_3GeMn(CO)_5$. [139]

The introduction of acetylene compounds at the M–M′ bond has also been studied [143]. Thus the photochemical reaction of perfluorobut-2-yne with $Me_3SnFe(CO)_2Cp$ in pentane leads to the formation of a 1 : 1 addition product:

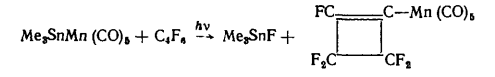


A similar reaction with $Me_3SnMn(CO)_5$ gives a cyclic insertion product:



The reaction of $Ph_3SnMn(CO)_5$ with perfluorobutyne proceeds with much greater difficulty and leads to the formation of a compound in very low yield, evidently also a 1 : 2 addition product.

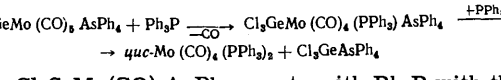
The reaction of $Me_3SnMn(CO)_5$ with perfluorocyclobutene involves breaking of the Sn–Mn bond:



3. Replacement of Carbonyl Groups by Other Ligands

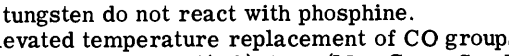
Derivatives of metal carbonyls containing a metal–Group IVB element bond can react with some nucleophilic reagents with the replacement of one or more CO groups.

Triphenylphosphine reacts with a Ge–Mo complex [123]:



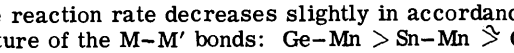
whereas $Cl_3SnMo(CO)_5AsPh_4$ reacts with Ph_3P with the simultaneous replacement of CO by phosphine and breaking of the Sn–Mo bond. The analogous derivatives of chromium and tungsten do not react with phosphine.

At elevated temperature replacement of CO groups in compounds of the $Ph_3MM'(CO)_5$ type (M = Ge or Sn, M′ = Mn or Re) by triphenyl-phosphine, -arsine, and -stibine takes place with the retention of the metal–metal bonds [22, 64, 71, 72] for example,



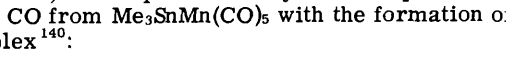
The reaction rate decreases slightly in accordance with the nature of the M–M′ bonds: Ge–Mn > Sn–Mn ≳ Ge–Re > Sn–Re. It is characteristic that the replacement of CO groups in compounds with a heteroatomic M–M′ bond proceeds more readily than in the corresponding dimeric carbonyls [144, 145].

Ethylene, unlike perfluoroethylene is capable of displacing CO from $Me_3SnMn(CO)_5$ with the formation of a π-complex [140]:



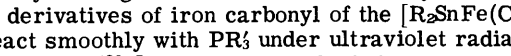
The germyl analogue does not react with ethylene [141]

The derivatives of iron carbonyl of the $[R_2SnFe(CO)_4]_2$ type react smoothly with PR'_3 under ultraviolet radiation, with formation [126–7] of a compound of the type $[R_2SnFe(CO)_3PR'_3]_2$. Depending on the ratio of the reagents both di- and mono-substituted products can be obtained [50, 84]:



where M = Sn or Pb; R = Et or Bu; and R′ = Et, Ph, or OMe.

The organopolymetallic derivatives of cobalt carbonyl are also capable of replacement of the CO groups. Phosphines react in heptane with the silicon and lead derivatives even at 25–50°C: [50, 69]



where M = Si or Pb; R = H, Et, or Cl; and R′ = Et or Ph.

When $Cl_2Sn[Co(CO)_4]_2$ is boiled with PPh_3 in THF a disubstituted product, $Cl_2Sn[Co(CO)_3PPh_3]_2$, is formed irrespective of the ratio of the initial reagents [90]. An analogous derivative of germanium was obtained [78] in THF at room temperature and also on boiling in hexane. At room temperature in hexane monosubstituted products of the type:

where M = Ge or Sn, are formed.

Hence all the organopolymetallic derivatives of metal carbonyls react with nucleophilic reagents with release of CO, unlike the alkyl derivatives of manganese, rhenium, and cobalt carbonyls $R–M'(CO)_X$ which in analogous reactions [146, 147] form acyl compounds of the $R–\overset{\overset{O}{\|}}{C}–M'(CO)_{X-1}L$ type. It has been found that [69] the introduction of CO at the M–M′ bond does not take place even at high carbon monoxide pressure. Evidently this phenomenon is connected with an increase in the strength of the M–M′ bonds owing to d_π–d_π interaction between the metal atoms [51, 81, 148]. This interaction can be represented schematically as a large contribution from resonance structure (IX):

Evidently the increased strength of the M–M′ bond in comparison with the C–M′ bond hinders the migration of the X_3M radical to the carbonyl group, as occurs with alkyl derivatives [149].

The fact that the replacement of CO groups in $Ph_3SnMn(CO)_5$ and $Ph_3GeMn(CO)_5$ leads to derivatives in which the phosphinic group is in the trans-position to the Ph_3M group [28, 150], whereas the corresponding organic derivatives of manganese and rhenium carbonyls have the *cis*-configuration [151, 152], mentoattention. Evidently apart from the steric factors electronic effects also play a part here. Possibly the presence of d_π–d_π interaction between the manganese and germanium or tin atoms, that is, the high contribution of structure (IX), determines the low strength of the bond of the axial carbonyl group with the metal in comparison with the equatorial ones.

Additional confirmation of the d_π–d_π metal–metal interaction can be seen in the increase in the rate of exchange of the CO groups for PPh_3 in compounds of the $X_2M[Co(CO)_4]_2$ type (where M = Ge or Sn) with increase in the electronegativity of X in the order Me < Ph < Cl. The introduction of substituents of greater electronegativity favours an increase in the electron-accepting power of the tin or germanium atoms leading to an increase in the multiplicity of the M–Co bonds and the weakening of the d_π–π^* Co–CO bonding.

V. PHYSICAL METHODS OF INVESTIGATION OF DERIVATIVES OF METAL CARBONYLS CONTAINING A METAL–METAL BOND

Physical methods of investigating compounds containing bonds between Group IVB elements and transition metals,

are used not only for finding or confirming the hypothetical structure of the molecules, but also give valuable information about the nature of the bonds in these compounds, which often cannot be obtained by purely chemical methods. The results of the X-ray structural investigation of the molecules of organopolymetallic compounds are given in Chapter II. The present chapter deals with the use of optical methods, radio and mass spectroscopy, and also the electrochemical investigation of compounds with M–M′ bonds.

1. Infrared Spectroscopy

The literature now contains information about the infrared spectra of most of the derivatives of metal carbonyls containing a bond between the transition metals and Group IVB elements.

The low-frequency range of the infrared spectra (700 to 100 cm^{-1}) of these compounds has been studied comparatively little and a precise assignment of the bands of the M–M′ and M′–CO stretching vibrations and M′–C–O deformation vibrations, which appear in this range, has not yet been made. In an analysis of the spectra of compounds of type $X_3GeMn(CO)_5$ and $X_2Ge[Mn(CO)_5]_2$ [150] the intense band at 470–450 cm^{-1} is assigned to ν^3_{Mn-C}, and the band in the 660–640 cm^{-1} range to δ_{CO}, by analogy with the assignment of the bands in the infrared spectra of $Mn_2(CO)_{10}$ [106,107] and $XMn(CO)_5$ (X = Cl, Br, I). [153] With increase in the electronegativity of X in the Ge–Mn compounds there is a decrease in the ν_{Mn-C} frequency. In the $Ph_3GeMn(CO)_4PPh_3$ spectrum there is a more significant increase in the ν_{Mn-C} frequency (by 55 cm^{-1}) and a decrease in the frequency of the C–O stretching vibrations, in comparison with the corresponding frequencies in the spectrum of the unsubstituted derivative, which confirms the close relation between the degree of $d_\pi - p^*_\pi$ bonding of M′–CO and of the π-bonding of the C–O groups.

Several papers [154–156] deal with the determination of the frequencies of the M–M′ stretching vibrations. It has been shown that the change in the $\nu_{M-M'}$ frequencies which appears in the 220–160 cm^{-1} range can be correlated with the corresponding changes in the frequencies of the C–O stretching vibrations. Usually, with an increase in the electronegativity of the substituent X in the compounds of type $X_{4-n}M[M'(CO)_xL]_n$, there is an increase in the $\nu_{M-M'}$ frequency which is consistent with increase in the $d_\pi - d_\pi$ interaction between the metal atoms.

The absorption range of the stretching vibrations of the CO groups (2200–1800 cm^{-1}) has been investigated most completely. X-ray diffraction investigations have shown that irrespective of the symmetry of the molecule as a whole in most of the compounds of the $X_{4-n}M[M'(CO)_xL]_n$ type a certain local symmetry of the metal carbonyl groups, found also for the corresponding derivatives of $XM'(CO)_xL$ type, where X is an organic radical or halogen atom, is mainly retained. It must therefore be expected that the infrared spectra of the derivatives or carbonyls which contain an M–M′ bond will be analogous to the spectra of the organohalogen derivatives of the corresponding metal carbonyls. Table 3 gives the theoretical and observable number of bands, ν_{CO}, for the organopolymetallic carbonyl compounds with various symmetries.

As Table 3 shows, the number of ν_{CO} bands in compounds which contain one $M'(CO)_xL$ group corresponds to the theoretical for the local symmetry of this group independently of the general symmetry of the molecule.

However, for compounds which contain several metal carbonyl groups there is always a greater number of bands. The appearance of additional bands in the spectra of these compounds can be connected with the interaction of the individual $M'(CO)_xL$ groups with one another. Furthermore allowance must be made for the decrease in the total symmetry of the molecules $X_{4-n}M[M'(CO)_xL]_n$ where $n > 1$ in comparison with the molecules of the compounds $X_3MM'(CO)_xL$.

Table 3. Number of bands of the stretching vibrations of the CO groups and their assignment in the infrared spectra of organopolymetallic derivatives of metal carbonyls.

Type of compound	Symmetry point group	Assignment of bands	Number of bands: theoretical	Number of bands: observed	Reference
Group VI					
$X_3MM'(CO)_3Cp$	C_{3v}	A_1+E	2	3	61, 135
$X_2M[M'(CO)_3Cp]_2$	C_{2v}		5		
	C_2, C_s, C_1		6	5–6	61, 135
Group VII					
$X_3MM'(CO)_5$	C_{4v}	$2A_1+E(+B_1)$	3–4	2–4	67, 150, 157
$X_2M[M'(CO)_5]_2$	C_{2v}	$3A_1+3B_1+B_2$	7	4–8	66, 150, 157
$XM[M'(CO)_5]_3$	C_{3v}	$3A_1+4E$	7	6–9	65, 66
Group VIII					
a. Iron derivatives					
$X_3MFe(CO)_3Cp$	C_{3v}	A_1+B_1	2	2	158, 159
$X_2M[Fe(CO)_2Cp]_2$	C_2	$2A+2B$	4	4	158, 159
	C_s	$2A'+2A''$	4	4	74, 158
	C_1	$4A$	4	4	
$(X_3M)_2Fe(CO)_4$	C_{2v}	$2A_1+B_1+B_2$	4	3	51
$[X_2MFe(CO)_4]_2$	D_{2h}	$B_{1u}+2B_{2u}+B_{3u}$	4	4	51
$X_4M_3[Fe(CO)_4]_4$	D_{2d}	$3B_2+4E$	7	4	51
$M[Fe(CO)_4]_4$	D_{2d}	$3B_2+4E$	7	4	51
b. Cobalt derivatives					
$X_3MCo(CO)_4$	C_{3v}	$2A_1+E$	3	3–4	81
	C_s	A_1+3A'	4	4	
$X_2M[Co(CO)_4]_2$	C_{2v}	$3A_1+3B_1+B_2$	7	7	81
	C_s	$4A'+4A''$	8	8	
$XM[Co(CO)_4]_3$	C_{3v}		7	6–8	80

It was found [158,159] that in compounds of the type $X_2M[Fe(CO)_2Cp]_2$ (where M = Ge or Sn) the picture of the νCO bands can change significantly with the nature of substituent X. X-Ray structural analysis of compounds of this type [39–41,43,44] showed that in the crystalline state they have C_2 or C_1 molecular symmetry. In solutions where the molecules are in a less sterically hindered state some change in the geometric configuration can be expected. In a study of the infrared spectra it was suggested that owing to rotation around the Ge–Fe bond and Sn–Fe bonds rotational isomers can exist in solutions, having C_2, C_1, or C_S symmetry depending on the electronic features and the volume of substituent X. For the compound $MeCl_2GeFe(CO)_2Cp$ the assumption of the existence of rotational isomers by rotation around the Ge–Fe bond was confirmed [159] in studying the effect of the polarity of the solvent and the temperature on the ratio of the intensities of the absorption bands.

On the basis of the assignment of the bands according to vibrational type, an analysis of the displacement of the corresponding bands as a function of the Group IVB element and the X substituents bound to them becomes possible.

In studying the infrared spectra of derivatives of the type $X_nR_{3-n}GeCo(CO)_4$ it was found[81] that there is a linear relation between the frequencies of the ν_{CO} bands and the total electronegativity of the halogen atoms bonded with the germanium. A similar dependence for the main frequency ν_{CO} was observed[50,120] in compounds of the $X_3SiCo(CO)_4$ type, where X = Et, Ph, OMe, or Cl. The existence of such a relation shows the connection between the charge on the atom of the non-transition Group IV element and the frequency ν_{CO} in all the derivatives of this type.

The nature of the change in the frequencies in the series of cobalt derivatives with the nature of the Group IVB element has been explained[50]. In the spectra of the compounds $Et_3MCo(CO)_4$ there is an almost linear decrease in the mean frequency ν_{CO} in the series of M: C > Si > > Ge > Sn > Pb. Since the electronegativities of Si, Ge, Sn, and Pb are similar[27] it can be suggested that the σ-components of the M–Co bonds should also always be similar. If that is so the decrease in the mean frequency ν_{CO} can be the result of a decrease in the π-transfer from the d_π-orbitals of the cobalt atom to the vacant d_π-orbitals of the non-transition element in the order Si > Ge > Sn > > Pb. Charge transfer in the M–Co π-system is confirmed by a study of the dipole moments of the complexes $X_3MCo(CO)_4$ and agrees with the values of the overlap integrals in these compounds[50].

The most convenient subjects for an analysis of the electronic effects of substituents bound to a transition metal atom are derivatives of Group VII metal carbonyls of the type $X_3MM'(CO)_5$ where M' = Mn or Re. Group theory predicts that in the infrared spectra of these compounds (point group symmetry C_{4V}) there should be three permitted bands ν_{CO}: $2A_1 + E$ and that the B_1 band should be active in Raman spectra[18,160,161]. Fig. 7 shows the vibration types.

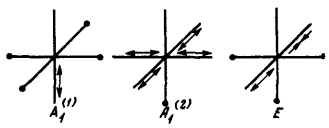


Figure 7. Types of vibrations of CO groups in $XM'(CO)_5$ and $X_3MM'(CO)_5$ (M' = Mn or Re) permitted in the infrared spectra. Only one component of the *E* vibrations is shown.

The band of type $A_1^{(1)}$, which has the lowest frequency, is assigned to the vibrations of the axial CO group. The most intense band of type *E* is assigned to the vibrations of the four equatorial groups. The bands of types $A_1^{(1)}$ and *E* often coincide. The $A_1^{(2)}$ vibrations are active in the infrared spectra only because of the non-coplanarity of the equatorial CO groups; this band of maximal frequency has low intensity and therefore is difficult to use in an analysis of the effects of substituents at the metal carbonyl group.

The study of the infrared spectra of the compounds of $XMn(CO)_5$ showed that there is a linear relation between the position of the type *E* bands and the Taft inductive parameter σ* for substituent X in the order: Me, H, Ph, I, CF_3, Br, Cl.[162] A similar change in frequency with the electronegativity of the substituent $R_nX_{3-n}M$ was also observed in the series of derivatives of type $R_nX_{3-n}MM'(CO)_5$, where M = Ge, Sn; M' = Mn or Re; R = Me or Ph; X = Cl or Br; and $0 \leq n \leq 3$.[67,150]

On the basis of an LCAO-MO examination of the bonds in the $XM'(CO)_5$ molecules (Chapter II) it can be assumed that inductive transfer in the molecules of type $X_3MM'(CO)_5$ should be reflected in the position of all the absorption bands of the CO groups, whereas the mesomeric effect associated with the transfer of electrons from $(n-1)d_{XZ}$ and d_{YZ} orbitals of the transition metal to the vacant d_π orbitals of the Group IVB element will affect only the vibration frequency of the axial carbonyl group.

The analysis of the infrared spectra of several compounds containing an M–M' bond which was made on the basis of this assumption showed[163] that there is a considerable $d_\pi - d_\pi$ interaction between the atoms of the Group VII element and the Group IVB element. The degree of π-bonding increases with increase in the electronegativity of the substituent connected with the transition metal atom. It was found that the degree of π-bonding for germanium compounds is greater than for analogous tin derivatives.

The direction of the inductive effect of the substituents X_3M in compounds with an M–M' bond varies on going from X = alkyl or aryl to X = halogen. The substituents Me_3M and Ph_3M are stronger electron donors than Me (and Ph), whereas the Cl_3M and Br_3M groups are comparable in their electron-acceptor properties with halogen atoms. There is some additivity in the increase in σ-acceptor properties of the $R_nX_{3-n}M$ groups with successive increase in the number of halogen atoms bound to the Group IVB element (Table 4).[150,163]

Table 4. Change in the σ- and π-effects in the series of $Ph_nBr_{3-n}GeMn(CO)_5$ compounds.

Compound	Frequency ν_{CO}, cm^{-1}			σ*	Δσ*	π	Δπ
	$A_1^{(1)}$	*E*	$A_1^{(2)}$				
$Ph_3GeMn(CO)_5$	2004	2004	2094	−0.45	0.97	1.73	0.51
$Ph_2BrGeMn(CO)_5$	2019	2019	2108	0.52	0.90	2.24	0.43
$PhBr_2GeMn(CO)_5$	2033	2033	2117	1.42	0.84	2.67	0.39
$Br_3GeMn(CO)_5$	2046	2046	2136	2.26		3.06	

The effect of the nature of the transition metal on the vibration frequency of the CO groups is much greater than the effect of the Group IVB element. In the series of isostructural derivatives of carbonyls of Group VI metals there is an increase in the mean frequency ν_{CO} with increase in the atomic number of the metal, for example, for $Ph_3SnM'(CO)_3Cp$[61] ν_{CO} is 1987, 1923, 1897 for M' = Cr; 2004, 1934, 1909 for M' = Mo; and 2014, 1927, 1902 cm^{-1} for M' = W. A similar increase in mean frequencies is observed also for derivatives of rhenium carbonyl compared with the corresponding manganese compounds[67,163].

The assignment of the ν_{CO} bands according to the types of vibrations in the spectra of the compounds which contain several metal carbonyl groups is difficult. Nevertheless, it has been shown[61,66,74,80,81,135,136,150,157–159] that with increase in the electron accepting ability of the substituents bound to the Group IVB element there is an increase in all the frequencies of the CO vibrations.

The literature contains information about the ultraviolet spectra of the carbonyl compounds containing an M–M′ bond, limited to the series of compounds $R_3MM'(CO)_3Cp$ (with M = Ge or Sn; M′ = Mo or W; R = Me or Ph),[61] but these results are too few and the observed picture too complex for a successful interpretation.

2. PMR Spectroscopy

As a result of the study of the PMR spectra of compounds of the $X_3SnM'(CO)_3Cp$ and $X_2Sn[M'(CO)_3Cp]_2$ type (M′ = Mo and W) [135] and also of $X_3MFe(CO)_2Cp$ and $X_2M[Fe(CO)_2Cp]_2$ [158,159] (M = Ge and Sn) it was found that the chemical shift of the protons of the cyclopentadienyl ring (in the τ-scale relative to Me_4Si) increases with decrease in the electronegativity of substituent X. In the series of $X_3GeFe(CO)_2Cp$ compounds [112] the value of τ increases with the change in X in the order: F < Cl < Br < I. These facts show the inductive transfer of the electronic effects of the substituents X through the M–M′ bond to the cyclopentadienyl ring.

For methylgermanes and methylstannanes of the $Me_{4-n}MX_n$ type there is a linear dependence of the quantity τ on the total Taft inductive parameter σ^*,[133,164] for example, τ_{CH_3} is 9.93 in Me_4Sn, 9.37 in Me_3SnCl, 8.84 in Me_2SnCl_2, and 8.35 in $MeSnCl_3$, which corresponds with an increase in the inductive withdrawal of electrons from methyl groups of the electron-accepting substituents at tin or germanium atoms. On the other hand, in the trimethylstannyl derivatives of metal carbonyls it is difficult to find any correspondence between the values of τ_{CH_3} and the nature of the metal carbonyl groups. A successive increase in the number of metal carbonyl groups in $Me_{4-n}Sn[M'(CO)_xL]_n$ molecules leads to a displacement of the signal of the methyl protons to the strong field side (see Table 5), which could be due to the electron-acceptor nature of the metal carbonyl groups.

In studying the change in the spin-spin coupling constants J(Sn–H) in compounds of the $Me_{4-n}SnX_n$ type with the electronegativity of X, the following hypothesis was used[165]: the Sn–H spin-spin coupling tends to be proportional to the s-character of the hybrid sp^3 orbitals of the tin used in the Sn–CH_3 bond and the s-character of the tin atom tends to be concentrated in orbitals directed towards electropositive substituents, according to Bent's rule [37,38]. Here it was also assumed that the change in substituent X only affects the electronic state of the tin atom whereas other parameters of the X–Sn–C–H system of bonds remain almost unchanged. In the $Me_{4-n}SnCl_n$ series with successive increase in the number of chlorine atoms the value of $J(^{119}Sn–H)$ gradually increases: Me_4Sn 54.0; Me_3SnCl 59.7; Me_2SnCl_2 71.0, $MeSnCl_3$ 100.0 Hz.[166] The successive replacement of the methyl groups by metal carbonyl groupings leads to a decrease in the value of J [61,66,67,87] (Table 5).

Proceeding from these assumptions the decrease in the value of J in Sn-metal carbonyl compounds in comparison with Me_4Sn can be treated as a decrease in the s-character of the tin orbitals in the Sn–CH_3 bonds and a corresponding increase in it in the bonds with the transition metal atoms. This serves as confirmation of the electron-donating nature of the metal carbonyl groups and of the considerable covalency of the Sn–M′ bonds in these compounds.

Table 5 shows that the value of J is much greater for compounds containing a $Co(CO)_4$ group. This can be explained by the somewhat greater electronegativity of the $Co(CO)_4$ group in comparison with that of the other metal carbonyl groups [66].

The conclusions drawn on the basis of the change in the constant J agree with the X-ray structural data (see Chapter II) which show the increase in the s-character of the Sn–M′ bonds (tendency $sp^3 \rightarrow sp^2$) with increase in the number of metal carbonyl groups in these compounds. Unfortunately there are few compounds for which both structural and PMR data are known.

Hence an analysis of the chemical shifts of the methyl protons and of the value of the spin-spin coupling constants J(Sn–CH_3) (Table 5) leads to directly contradictory results. However, since the interpretation of the change in the constants J agrees with the conclusions from a study of the infrared spectra, and with the X-ray structural data, this characteristic evidently more correctly reflects the properties of the metal carbonyl groups. The contradiction arising in the treatment of the chemical shifts can be connected with the considerable extent of the M′–Sn–C–H chain and also with several other factors which influence the screening of protons.

An example of the use of PMR spectra for determining the composition of compounds and of finding the mechanism of reaction of the metal carbonyl compounds is the work of Nesmeyanov and coworkers [112] where the analysis of the displacement of signals of protons and the change in their intensity in compounds of the type $X_3GeFe(CO)_2Cp$ (X = Br, I) demonstrated exchange between the halogen atoms bound to a germanium atom (see Chapters III and IV).

Table 5. PMR spectra of methylstannyl derivatives of metal carbonyls.

Compounds of the $Me_{3-n}Cl_nSnM'(CO)_xCp$ type	τ	J(Sn–H), Hz	Compounds of the $Me_{2-n}ClSn[M'(CO)_xCp]_2$ type	τ	J(Sn–H), Hz	Compounds of the $MeSn[M'(CO)_xCp]_3$ type	τ	J(Sn–H), Hz
$Me_3SnMo(CO)_3Cp$	9.52	49.0	$Me_2Sn[Mo(CO)_3Cp]_2$	9.15				
$Me_2ClSnMo(CO)_3Cp$	9.02	47.7	$Me_2Sn[Mo(CO)_3Cp][Mn(CO)_5]$		36.9			
$Me_2SnW(CO)_3Cp$		48.7	$Me_2Sn[W(CO)_3Cp][Mn(CO)_5]$		37.3			
$Me_2SnMn(CO)_5$	9.54	48.3	$Me_2Sn[Mn(CO)_5]_2$	9.17	36.7	$MeSn[Mn(CO)_5]_3$	8.62	~24
$Me_2ClSnMn(CO)_5$	9.06	45.8						
$Me_2SnRe(CO)_5$	9.58	46.7	$Me_2Sn[Re(CO)_5]_2$	9.14	36.7	$MeSn[Re(CO)_5]_3$	8.43	24.7
$Me_2SnFe(CO)_2Cp$	9.55	49						
$Me_2ClSnFe(CO)_2Cp$	8.55							
$Me_2SnCo(CO)_4$	9.37	45.8	$Me_2Sn[Co(CO)_4]_2$	8.88	45.7	$MeSn[Co(CO)_4]_3$	8.98	33.0
		52.6						
			$MeClSn[Co(CO)_4]_2$	8.48				

Values given for J ($^{119}Sn–CH_3$).

3. Nuclear Gamma Resonance

Confirmation of the electron donating nature of the metal carbonyl groups in compounds containing a bond between the tin and transition metal atoms was obtained from nuclear gamma resonance spectra (Mössbauer effect)[167-169].

Table 6. Chemical shift* of the resonance of ^{119}Sn in the compounds $Ph_{4-n}Sn[Re(CO)_5]_n$ and $Ph_{4-n}Sn[Fe(CO)_2Cp]_n$.[167,168]

Compound	Chemical shift, δ, mm s^{-1}	Compound	Chemical shift, δ, mm s^{-1}
Ph_4Sn	1.11	Ph_4Sn	1.11
$Ph_3SnRe(CO)_5$	1.45	$Ph_3SnFe(CO)_2Cp$	1.48
$Ph_2Sn[Re(CO)_5]_2$	1.70	$Ph_2Sn[Fe(CO)_2Cp]_2$	1.74
$PhSn[Re(CO)_5]_3$	1.75	$PhSn[Fe(CO)_2Cp]_3$	2.00
		$Sn[Fe(CO)_2Cp]_4$	2.14

*Relative to SnO_2.

In the nuclear gamma resonance spectra of the compounds of the $R_{4-n}Sn[M'(CO)_xL]_n$ type, where $M'(CO)_xL$ = $Mn(CO)_5$, $Re(CO)_5$, or $Fe(CO)_2Cp$, and R = alkyl or phenyl, quadrupole splitting of the ^{119}Sn signal is absent, which shows the high degree of covalency of the metal–metal bond. In compounds which contain the $Co(CO)_4$ group quadrupole splitting occurs but to a lesser extent than the splitting brought about by the introduction of halogen atoms at the tin atom. This is additional confirmation of the high electronegativity of $Co(CO)_4$ in comparison with the other metal carbonyl groups.

Table 7. Nuclear gamma resonance spectra of the compounds $X_2Sn[Fe(CO)_2Cp]_2$.

X	^{119}Sn		^{57}Fe	
	δ, mm s^{-1}	Δ, mm s^{-1}	δ, mm s^{-1}	Δ, mm s^{-1}
Et	1.74	0	0.373	1,88
Me	1.68	0	0.378	1,715
Cl	1.94	2.37	0,361	1,64

In the spectra of the compounds $X_{4-n}Sn[M'(CO)_xL]_n$ (where M' = Mn, Re, Fe, Co; and X = Me, Et, Ph, Cl, or Br) there is a gradual increase in the chemical shift of the δ resonance of ^{119}Sn with increase in the number of metal carbonyl groups (see Table 6), which can be regarded as the consequence of the decrease in the ionicity of the bond due to the electron-donating nature of the metal carbonyl groups.

A comparison of the results[171] from nuclear gamma resonance spectra of the $X_2Sn[Fe(CO)_2Cp]_2$ compounds relative to both ^{119}Sn and ^{57}Fe shows that the substituent X at the tin atom affects the electron density of both metal atoms (Table 7).

4. Mass Spectroscopy

Information about the comparative strength of metal–ligand bonds and about the energies necessary for breaking these bonds can be obtained from the mass spectra of organopolymetallic compounds.

In the fragmentation of metal carbonyl derivatives with M–M' bonds competing processes can take place: removal of CO, loss of ligand containing a Group IVB element as an entity, and also the removal of a part of the ligand from the Group IVB atom and transfer of an atom or group of atoms from the ligand to the transition metal. For example, in the mass spectrum of $Ph_3SnMn(CO)_5$ peaks are observed which correspond with the ions: Ph_3SnMn^+, Ph_3Sn^+, $PhMn^+$, HMn^+, and Mn^+, and in the mass spectra of $PhBr_2SnMn(CO)_5$ there are peaks of $PhBr_2SnMn^+$, $PhSn^+$, $BrMn^+$, $PhMn^+$, HMn^+, and Mn^+.[170]

An investigation of the derivatives of molybdenum[171], manganese and rhenium[66,170,172], iron[172], and cobalt[79,80] carbonyls of the type $X_{4-n}M[M'(CO)_xL]_n$ showed that the fragmentation of these compounds occurs first with the successive removal of ligands (CO and Cp) from the transition metal atom. For compounds which contain several metal carbonyl groups fragmentation proceeds with gradual removal of these groups. The M–M' bond is broken, usually last of all. Thus in the mass spectrum of $ClSn[Mn(CO)_5]_3$ peaks for the presence of $ClSnMn_3(CO)_x^+$ (x = 0, 3–6, 8–11, 15), $ClSnMn_2(CO)_x^+$ (x = 0, 3, 5, 9, 10), $SnMn(CO)_x^+$ (x = 0, 45) have been noted. Hence under the conditions for measuring the mass spectra the M–M' bond exhibits greater stability than the M–X bond and still greater than the M'–CO or M'–Cp bonds. With increase in the number of metal carbonyl groups attached to the atom of the Group IVB element, the strength of the M–M' bonds decreases which agrees with the chemical properties and with the increase in the length of these bonds observed in the structural investigations.

With the aid of mass spectroscopy it was shown that the structure of compounds of the $XSn[Co(CO)_4]_3$ type corresponds with structure (VII) (see Chapter III).[79,80] In the fragmentation of these compounds a considerable proportion of ions formed as a result of the breaking of the Sn–Co bonds was observed, which could mean that the $SnCo_3$ skeleton is weaker than that of $SnMn_3$.[66]

Mass spectroscopy is very valuable for finding the structure of the products formed by the introduction of perfluoroacetylenes at Sn–Mn and Sn–Fe bonds[143] (see Chapter IV).

5. Polarography

Polarographic reduction of a series of metal carbonyl derivatives with M–M' bonds[173-176] allowed the relative polarisation of these bonds to be estimated. The reduction of compounds of this type is always accompanied by breaking of the M–M' bond, which leads to the formation of anions containing a transition metal atom.

$$R_3M{-}M'(CO)_xL \xrightarrow{+1e} R_3M^{\cdot} + [:M'(CO)_xL]^- \quad (A)$$

$$R_3M{-}M'(CO)_xL \xrightarrow{+2e} R_3M^-: + [:M'(CO)_xL]^- \quad (B)$$

When M = Sn and R = Me or Ph the reduction has a single-electron nature (scheme A), whereas phenyl derivatives are reduced at more negative potentials than the methyl derivatives. When M = Pb the reduction proceeds by scheme (B) with the formation of two anions.

The ease of reduction varies in the following sequence:

$$Sn{-}Co > Et_3Pb{-}Mn > Me_3Sn{-}Mn = Me_3Sn{-}Mo > Ph_3Pb{-}Mn = Ph_3Pb{-}Fe > Ph_3Pb{-}Mo > Ph_3Pb{-}Re = Ph_3Sn{-}Mo > Ph_3Sn{-}Mn = Ph_3Sn{-}Re > Ph_3Sn{-}Fe.$$

The reduction of the compounds $Me_2Sn[Mo(CO)_3Cp]_2$ and $Me_2Sn[Fe(CO)_2Cp]_2$ leads to the loss of both metal carbonyl groups as anions:

$$Me_2Sn[M'(CO)_xCp]_2 + 2e \rightarrow Me_2Sn + 2[:M'(CO)_xCp]^- .$$

The reduction potential of the compound with Sn–Fe bonds here is higher than for the Sn–Mo bond.

In the reduction of the compound

$$[Cp(OC)_3Mo]_2Sn[Fe(CO)_2Cp]_2$$

which contains different transition metal atoms, a more complex picture is observed. Evidently loss of the Mo fragment takes place first and then a system with an Fe–Sn–Sn–Fe chain is formed.

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Institute of Organoelemental Compounds,
Academy of Sciences of the USSR, Moscow

U.D.C. 547.253

Effect of Electron-donor Solvents on the Reactivity of Lithium Alkyls

E.A.Kovrizhnykh and A.I.Shatenshtein

The causes of and the relations governing the acceleration of reactions involving lithium alkyls by electron-donor solvents are discussed. The kinetic effect is due to a change in the polarity of the C-Li bond in consequence of the formation of complexes (of the donor-acceptor type) of the lithium alkyl and the solvent and a change in the state of lithium alkyl in solution.
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I. INTRODUCTION

Despite the exceptionally wide applications of lithium alkyls in synthetic organic and polymer chemistry, it is still not quite clear how the state of lithium alkyls changes under the action of different solvents; the problem of the form in which lithium alkyls participate in reactions and of the ultimate mechanism of the change in the reactivity of lithium alkyls under the influence of electron-donor solvents remains controversial. These problems are discussed in the present review†.

I. EFFECT OF SOLVENTS ON THE DEGREE OF ASSOCIATION OF LITHIUM ALKYLS IN SOLUTION

The co-ordination unsaturation of organolithium compounds[1-3] is reflected in their characteristic capacity for association. Thus in hydrocarbon solvents ethyl- and n-butyl-lithium exist in the form of hexamers and t-butyl-lithium in the form of a tetramer (see Refs. 1 and 5). Branching or an increase in the length of the alkyl group R inhibit the association RLi.[4,6]

In connection with the problem of the effect of electron-donor solvents on the reactivity of lithium alkyls, information about their complexes with ethers[7-10], amines[11-13], and dialkyl sulphides[14] is of interest. The structure of such complexes has still not been adequately investigated and there are discrepancies in the data on their composition[10-12,15]. For example, Brown et al.[12] believe that, in benzene solutions containing a large excess of triethylamine relative to ethyl-lithium, a 1 : 1 complex is formed, which is a dimer of ethyl-lithium solvated by two molecules of the base. On the other hand, according to Eastham and coworkers[10,11,15], complexes of lithium alkyls and solvents with one electron-donor atom (triethylamine, ethyl ether, tetrahydrofuran) have a 2 : 1 composition, corresponding to a dimer of the lithium alkyl solvated by one molecule of the amine or ether, even in the presence of a large excess of the solvent. Complex formation with an electron-donor substance D can be represented by the mechanism[15]

$$[(RLi)_2]_n + n\,D \rightarrow n\,(RLi)_2 \cdot D. \qquad (1)$$

In the complex formation process, steric factors play an important role, which is very characteristic of the specific solvation of cations[16]. Thus although triethylamine is a stronger base than tetrahydrofuran (THF),[17,18] the steric hindrance to solvation[11,19,20] makes the complexes of RLi with triethylamine less stable and less polar than those with THF.[11]

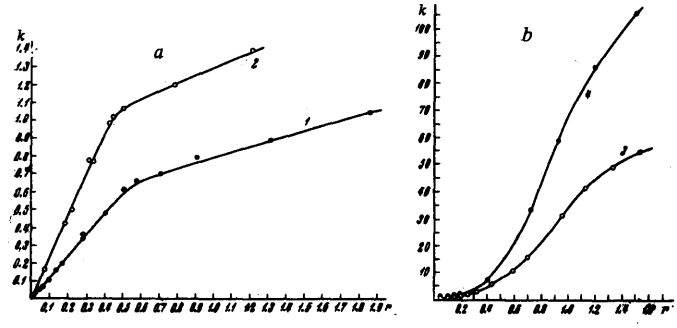

Figure 1. Determination of the composition of n-butyl-lithium solvate from data on the kinetics of the reaction between n-butyl-lithium and n-butyl bromide. Variation of k with r: *a*) for ethyl ether (*1*) and tetrahydrofuran (*2*); *b*) for 1,2-diethoxyethane (*3*) and 1,2-dimethoxyethane (*4*).

Information about the composition of complexes of lithium alkyls with electron-donor solvents can be obtained indirectly in some cases by studying the kinetics of reactions in which the lithium alkyls participate. For example, when the rate of reaction n-butyl-lithium with n-butyl bromide[21] (A) or 1-bromo-octane[22] (B) is studied, the curve relating the rate constant k to the molar ratio r of ether and the lithium alkyl in hexane solution shows an inflection of r = 0.5 (Fig. 1*a*). This indicates the formation of 2 : 1 complexes of n-butyl-lithium with ethyl ether or tetrahydrofuran.

When the reaction of A is carried out with addition of variable amounts of ethylene glycol ethers, each of which contains two oxygen atoms, the concentration dependence of the rate constant has a different form (Fig. 1*b*). The rate constant increases in proportion to the square of the concentration of the ether (c) up to r close to unity This can

† For an exhaustive list of the literature references on the properties and reactions of lithium alkyls, see Talalaeva and Kocheshkov[1].

be satisfactorily explained if it is supposed that in this case 1 : 1 complexes of n-butyl-lithium with the ethylene glycol ether are active in the reaction of n-butyl-bromide with n-butyl-lithium (see also Ref. 23). The different orders of reaction with respect to the ether (first in the case of ethers with one oxygen atom and second when the ether molecule contains two oxygen atoms, Fig. 2) correspond to different compositions of the complexes.

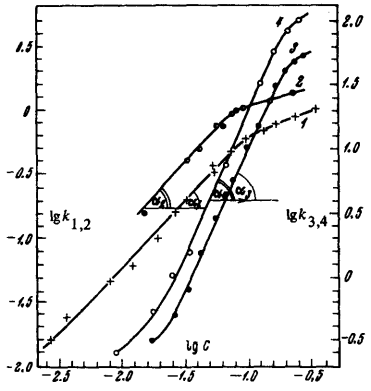

Figure 2. Determination of the order of the reaction between n-butyl-lithium and n-butyl bromide with respect to ethyl ether (*1*), tetrahydrofuran (*2*), 1,2-diethoxyethane (*3*), and 1,2 dimethoxyethane (*4*). (tan $\alpha_1 \simeq$ tan $\alpha_2 \simeq 1$; tan $\alpha_3 \simeq$ tan $\alpha_4 \simeq 2$).

Infrared spectra[4,6,24,25] and NMR (^{1}H and ^{7}Li) spectra[4,15,26] show that the degree of association of lithium alkyls in electron-donor solvents is lower than in hydrocarbon solvents. A reliable determination of the degree of association of lithium alkyls in ether solutions is complicated by the fact that lithium alkyls can react irreversibly with ethers[27-30]‡. Nevertheless, knowledge of the state of lithium alkyls in electron-donor solvents is important not only in understanding the characteristics of the kinetics and mechanisms of their reactions in these media but also because it throws light on the mechanism of the decomposition of association complexes under the action of electron donors.

The decomposition of association complexes is frequently represented by the equation

$$\frac{1}{n}(RLi)_n \rightleftarrows RLi, \qquad (2)$$

which reflects the process occurring, albeit of course in a simplified form. In more realistic hypotheses[34,35] it is postulated that the dissociation of the organolithium complexes is stepwise and is represented by equations of the type

$$(RLi)_n \rightleftarrows (RLi)_{n-1} + RLi. \qquad (3)$$

‡ The rate of decomposition depends on the structure of both reactants[24,27]. This reaction affects significantly the polymerisation processes initiated by lithium alkyls[31-33] and in principle can distort the kinetics of other reactions of lithium alkyls in the presence of ethers.

Thus it is suggested that association complexes of different composition are present in solution in equilibrium with one another and with the monomeric form of the lithium alkyl. This widely held view was objected to by Brown[36], who believes that not all the association complexes are stable in solution. On the basis of NMR (^{7}Li and ^{1}H) spectra, Brown concluded[26] that ethyl- and methyl-lithium have a tetrameric structure in ethyl ether at low temperatures. According to his experimental data for the kinetics of the intermolecular exchange of the alkyl groups of ethyl- and methyl-lithium association complexes in ethyl ether[26] and the association complexes of ethyl-lithium in toluene[37], the rate of this reaction in the hydrocarbon solvent is determined by the breakdown of lithium-alkyl hexamers:

$$(RLi)_6 \rightarrow (RLi)_4 + (RLi)_2, \qquad (4)$$

and in ethyl ether by the breakdown of the tetramer with formation of the dimer:

$$(RLi)_4 \rightarrow 2\,(RLi)_2\,. \qquad (5)$$

In another study[12] Brown investigated cryoscopically the mechanism of the successive breakdown of ethyl-lithium hexamers into tetramers and dimers following the addition of triethylamine to the benzene solution. According to Brown, in the region of low molar ratios of the electron-donor solvent (D) and lithium alkyl the solvation of the hexamer $[(RLi)_6 + 2D \rightarrow (RLi)_6.2D]$ does not result in its breakdown, but in the presence of an excess of the base the hexamer is completely dissociated into the solvated dimer.

Eastham and Gibson inferred the changes in the state of a number of lithium alkyls in different mixtures of an ether or amine with n-hexane from a study of the dielectric constant[10,11], the NMR spectra[10,15], or the vapour pressure of ethyl ether over the solution[10] as a function of its content of the electron-donor solvent. The curves for the above relations have an inflection or break on attainment of a 1 : 2 molar ratio of the electron-donor additive to the lithium alkyl. The subsequent form of the curves showed that, after further increase of the concentration of the ether or amine in solution, the state of the lithium alkyl did not alter significantly. Eastham and Gibson's conclusion[10,15] concerning the dimeric structure of n-butyl- and isobutyl-lithium in ethyl ether and in tetrahydrofuran cannot be regarded as unambiguous. Their results provide evidence only concerning the ratio of the number of moles of the ether (amine) and the lithium alkyl in the solvate complexes.

More reliable information about the degree of association of lithium alkyls in ethereal solutions (at room temperature) was obtained recently by West and Waack[38] by an isopiestic method. The degree of association of methyl- and phenyl-lithium in tetrahydrofuran at 75°C proved to be respectively 4 and 2, benzyl-lithium was not associated under these conditions, and in ethyl ether methyl- and n-butyl-lithium are tetrameric. Furthermore, Brown's[12] and Eastham's[10,15] conclusions are inconsistent with the data of Waack and coworkers[38,39] on the kinetics of the reactions of lithium alkyls with 1 : 1-diphenylethylene and triphenylmethane in ethyl ether and tetrahydrofuran at room temperature. The order of these reactions with respect to methyl- and n-butyl-lithium is close to 3.

Thus not only in hydrocarbon but also in ethereal solutions lithium alkyls are associated, which is evidence of considerable stability of their association complexes. The information about the true state of lithium alkyls under different conditions requires further revision.

II. KINETICS OF REACTIONS OF LITHIUM ALKYLS IN HYDROCARBON SOLUTIONS

The interpretation of data on the kinetics of reactions of lithium alkyls in solutions is far from simple. Any kinetic mechanism must take into account the association of the lithium alkyl. Until recently it was believed that in all cases only the monomer of the lithium alkyl, in equilibrium with association complexes, is reactive. This equilibrium is represented in Scheme 1, where the equation for the rate of reaction of RLi with a substrate S under the conditions of such equilibrium[4] is also included.

Scheme 1

$$(RLi)_n \overset{K_e}{\rightleftarrows} n\,RLi\,,$$

$$K_e = \frac{[RLi]^n}{\left(\frac{[RLi]_0}{n}\right)},$$

$$RLi + S \rightarrow \text{reaction product},$$

$$V = k_1[S][RLi] = k_1 K_e^{1/n}\left(\frac{[RLi]_0}{n}\right)^{1/n}[S] = k_{overall}[S][RLi]_0^{1/n}.$$

Here and henceforth V represents the rate of reaction and the subscript 0 denotes the initial concentration.

Apart from the widely adopted mechanism in Scheme 1, Brown[4] postulates three further possible reaction mechanisms in which the lithium alkyl reacts as the association complex.

Scheme 2

$$(RLi)_6 \overset{K_e}{\rightleftarrows} (RLi)_4 + (RLi)_2\,,$$

$$K_e = \frac{[(RLi)_4][(RLi)_2]}{[(RLi)_6]},$$

$$(RLi)_2 + S \rightarrow \text{reaction product} + RLi\,,$$

$$V = k[(RLi)_2][S] = kK_e^{1/3}[(RLi)_6]^{1/3}[S] = k_{overall}[RLi]_0^{1/3}\,.$$

Scheme 3

$$(RLi)_6 + S \overset{K_e}{\rightleftarrows} (RLi)_6S\,,$$

$$K_e = \frac{[(RLi)_6\cdot S]}{[(RLi)_6][S]} = \frac{[c]}{([S]_0 - [c])([H]_0 - [c])},$$

where $[c] = [(RLi)_6.S]$ and $[H]_0$ is the initial concentration of the hexamers:

$$[c] \approx \frac{K_e\cdot[S]_0\cdot[H]_0}{1 + K_e\cdot([H]_0 + [S]_0)}$$

If K_e is small, then $[c] \simeq K_e[S]_0[H]_0$ and $V = k[c] = kK_e[S]_0[H]_0$.

If $[S]_0 \gg [H]_0$ and $K_e[S]_0 \gg 1$, then $[c] \simeq [H]_0$ and $V = k[H]_0$.

If $[H]_0 \gg [S]_0$ and $K_e[H]_0 \gg 1$, then $[c] \simeq [S]_0$ and $V = k[S]_0$.

Scheme 4

$$(RLi)_6 \rightarrow (R_5Li_6)^+ + R^-\,.$$
$$R^- + S \rightarrow \text{reaction product}\,.$$

In Schemes 1–4 the possible reaction pathways by a heterolytic mechanism are postulated. It should be noted that in a hydrocarbon medium lithium alkyls may react also by a homolytic mechanism, for example, with alkyl halides[40].

According to Brown[4], Scheme 4 should be excluded from consideration as in this case the interaction of the substrate with RLi requires an unduly high activation energy.

Scheme 1 shows that the order of the reaction with respect to lithium alkyl is equal to the reciprocal of its degree of association. In many studies on the kinetics and the initiation of polymerisation by n-butyl-lithium[41] and also on its reactions with 1,1-diphenylethylene[42] and fluorene[43] the order with respect to lithium alkyl proves to be 1/6, which is satisfactorily consistent with data on the degree of association of n-butyl-lithium in hydrocarbons[35]. The principal association complex of t-butyl-lithium in hydrocarbon solutions in the tetramer[44] and, in agreement with this, the reaction order with respect to this lithium alkyl in reactions with fluorene and 1,1-diphenylethylene is close to 1/4.[45]

However, in many cases the agreement of the results with the above mechanism is poor. For example, Ziegler and coworkers[46] already established that the reactions of ethyl-, n-propyl-, and n-butyl-lithium with 1,1-diphenylethylene in a hydrocarbon is of first order with respect to each reactant. West and Glaze[47] arrived at a similar conclusion for the reaction of ethyl-lithium with benzyl chloride in benzene. The data on the kinetics of the reaction of ethyl-lithium with 1,1-diphenylethylene obtained by Brown[4] are inconsistent either with the results of Ziegler[46] or those of Evans and George[42], since the reaction order with respect to ethyl-lithium proved to be variable in the range 0.7–0.95. In reactions involving the metallation of fluorene with ethyl-lithium and the addition of the latter to 1,1-diphenylethylene in benzene solutions, a low order (1/9) with respect to ethyl-lithium was observed[48], although it is known that its degree of association in benzene is 6.[12,49]

Data inconsistent with Scheme 1 are also found in the literature on anionic polymerisation. Thus Hsieh[50] showed that the rate of initiation of the polymerisation of styrene, butadiene, and isoprene is directly proportional to the concentration of the lithium alkyl in hydrocarbon solutions. Worsfold and coworkers[51,52] observed a variable reaction order (0.5–1) with respect to n-butyl-lithium in the polymerisation of the same monomers in cyclohexane. Finally, we may point out the discrepancy between the results of O'Driscoll et al.[53] and Worsfold and Bywater[41] for the degree of association of n-butyl-lithium and benzene if the latter is estimated from the order of the initiation reaction in the polymerisation of styrene. At styrene concentrations in excess of 0.5 M the order is 1/3,[53] while at concentrations less than 0.03 M it is 1/6.[41] Brown[4,36] expressed doubts concerning the universality of the kinetic mechanism in Scheme 1, mainly in its principal postulate that only the monomeric form of the lithium alkyl participates in the reaction. The concentration of the monomer RLi in a hydrocarbon solution must be extremely low. At best, only the dimer of the lithium alkyl, formed by reaction (4), can be present in appreciable amounts. If, on the other hand, the monomer RLi is nevertheless the active species, the reaction rate is limited by the stage involving the dissociation of the dimer into the monomer:

$$(RLi)_2 \rightarrow 2\,RLi\cdot \qquad (6)$$

According to Brown's estimate[36], a reaction with participation of the monomer RLi is possible when the heat of dissociation of the dimer does not exceed 20 kcal mole^{-1}. He suggests that the enthalpy of association of $(RLi)_2$ is not less than the value established by Morton[54] for the dimer of polyisoprenyl-lithium (37 kcal mole^{-1}). In addition, Brown refers to data[55] on the heat of dissociation of the dimer of trialkylaluminium, which is 20.2 kcal mole^{-1}, and notes that the heat of dissociation of $(RLi)_2$ must be appreciably higher, since, in contrast to trialkylaluminium, lithium alkyls are associated in ethereal solutions[2].

Without rejecting the possibility of reactions with participation of lithium alkyl by Scheme 2, Brown believes Scheme 3 to be more likely. He showed previously[12] that

the hexamer of a lithium alkyl is capable of forming complexes with Lewis bases. Brown assumed that such complexes are naturally formed also with less basic nucleophiles: alkyl halides, olefine, and other compounds. The apparent order of the reaction with respect to RLi and the substance reacting with it depends on their relative contents in the solution and on the equilibrium constant K_e for the formation of the complex of the lithium alkyl and the substrate. Studies on polymerisation initiated by lithium alkyls have been carried out over a wide range of relative concentrations of RLi and olefins. Therefore Brown believes that the above examples of discrepancies between different data on the order of the polymerisation initiation reaction are not surprising.

Brown's critical comments concerning Scheme 1 were objected to by certain workers[56,57], who pointed out the errors in Brown's calculation based on Morton's incorrect data for the heat of association of polyisoprenyl-lithium and its degree of association, which is actually four[34,51] and not two[54]. Furthermore, it was pointed out[56,57] that Scheme 1 is as a rule inapplicable in those cases where the solvent is not an aromatic but an aliphatic hydrocarbon.

In contrast to aliphatic hydrocarbons, aromatic hydrocarbons are apparently capable of solvating lithium alkyls, albeit only to a slight extent, by virtue of the formation of π-complexes[34,53]. This is shown by the comparison of both polymerisation rates in these and other solvents[34,50,57] and the ultraviolet spectra of solutions of s-butyl-lithium in benzene and in cyclohexane[57]. The variable reaction order with respect to the lithium alkyl and the S-shape of the kinetic curve for the initiation stage observed in aliphatic hydrocarbons[51,52,57] have been explained by the autocatalysis of the reaction as a result of the formation of cross-association complexes of the lithium alkyl and the product of its addition to the monomer[56,57].

These considerations[56,57] refer to the initiation stage and the polymerisation under the influence of lithium alkyls. The problem of the applicability of Scheme 1 to various reactions of associated organolithium compounds in hydrocarbon media still remains open.

III. EFFECT OF ELECTRON-DONOR SOLVENTS ON THE KINETICS OF REACTIONS OF LITHIUM ALKYLS

1. General Postulates

The powerful effects of electron-donor solvents on the reactivity of lithium alkyls was noted a long time ago. Ziegler[46] already pointed out the much higher rate of addition of n-butyl-lithium and other lithium alkyls to the double bond of 1,1-diphenylethylene in ethyl ether compared with the benzene solution. In tetrahydrofuran the reaction is almost instantaneous[58].

When even small amounts of ether or an amine are added to the hydrocarbon solvent, the initiation stage of the polymerisation of styrene or diene hydrocarbons by the lithium alkyl is also greatly accelerated[51,59-62] and to a much greater extent than the chain propagation stage[51,54,62,63]. The effect of ethers and amines on the kinetics of the initiation stage of the polymerisation by lithium alkyls has not as yet been investigated adequately in a quantitative sense because of the high rates of this stage in the presence of electron-donor additives[58,60-62].

There are literature data concerning the activating effect of electron-donor solvents also on other reactions of lithium alkyls, for example the metallation of hydrocarbons by them or their interaction with alkyl and aryl halides. According to Gilman's data[64,65], metallation by lithium alkyls is facilitated on passing from solutions in hydrocarbons to solutions in ethyl ether and in particular to solutions in tetrahydrofuran, which has been confirmed by Waack[66]. The nucleophilic activity of lithium alkyls increases even more under the influence of bistertiary amines[67]. The complex of n-butyl-lithium with *NNN'N'*-tetramethylethylenediamine readily metallates toluene and benzene even at a moderate temperature.

The reactions of organolithium compounds with alkyl and aryl halides are usually considered from the standpoint of organic synthesis. The number of kinetic studies which provide information about the effect of electron-donor solvents on reactions of this type is small. Ziegler[68] noted that the half-life of the reaction between n-butyl-lithium and n-butyl bromide decreased by a factor of 20 when it was carried out in ethyl ether instead of benzene. The rates of this reaction differ by more than 4 powers of 10 between n-hexane and its mixture with 1,2-dimethoxyethane for an equimolar content of the ether and the lithium alkyl[21]. In ethyl ether n-butyl-lithium reacts with 1-bromo-octane almost 800 times faster than in n-hexane[22].

The solvent can change not only the rate of reaction or its order with respect to the lithium alkyl[39,42,43,58] but the actual reaction path. The change in reaction order under the influence of the solvent is readily understood, since the state of the lithium alkyl in solution depends on the solvent. It is also known that, depending on the type of reactants and the reaction conditions, in particular the solvent, the organolithium compound reacts with alkyl and aryl halides[15,40,69] either by a heterolytic mechanism—the Wurtz reaction [reaction (7)] and the exchange of alkyl radicals [reaction (8)] are of this type—or by a homolytic mechanism [reaction (9)]:

$$R'Li + R''X \rightarrow R'R'' + LiX, \quad (7)$$

$$R'Li + R''X \rightarrow R'X + R''Li, \quad (8)$$

$$R'Li + R''X \rightarrow R'^{\cdot} + Li^{+} + R''^{\cdot} + X^{-} \quad (9)$$

The postulate that the reaction path can change is well illustrated, for example, by the data of Hoeg and Lusk[70], who investigated the reaction of n-butyl-lithium with n-benzyl chloride in several solvents. In ethyl ether and in n-hexane these reactants interact with formation of dibenzyl (I) and *p*-pentylbenzene (II):

$$C_6H_5CH_2Cl \xrightarrow[Et_2O(hexane)]{n\text{-}C_4H_9Li} [C_6H_5CH_2Li] \begin{cases} \xrightarrow{+C_6H_5CH_2Cl} C_6H_5CH_2CH_2C_6H_5 \ (I) \\ \xrightarrow[+n\text{-}C_4H_9Li]{} C_6H_5C_5H_{11} \ (II) \end{cases} \quad (10)$$

When the same reaction was carried out in tetrahydrofuran at room temperature, *trans*-stilbene was obtained in a yield of about 20% in addition to compounds (I) and (II). If the reaction follows the second pathway, then α-chlorodibenzyl (IV) and the carbanion of benzyl chloride (III) are formed as intermediates:

$$C_6H_5CH_2Cl \xrightarrow[THF]{+n\text{-}C_4H_9Li} \underset{(III)}{[C_6H_5\bar{C}HCl\overset{+}{Li}]} \xrightarrow{+C_6H_5CH_2Cl} \rightarrow \underset{(IV)}{C_6H_5CHClCH_2C_6H_5} \xrightarrow{+n\text{-}C_4H_9Li} C_6H_5CH{=}CHC_6H_5 + C_6H_5\underset{|}{\overset{C_4H_9}{C}}HCH_2C_6H_5 \quad (11)$$

An additional example is provided by data[71] on the change in the mechanism of the initiation by n-butyl-lithium of the polymerisation of methyl acrylate and methyl methacrylate when n-hexane is replaced by tetrahydrofuran.

The above findings by no means exhaust the literature data on the effect of solvents on the reactivity of lithium alkyls (see, for example, Bilevich and Okhlobystin[72]).

2. The Causes and the Principal Relations Governing the Effect of Electron-donor Solvents on the Kinetics of Reactions of Lithium Alkyls

The acceleration of the reactions of lithium alkyls in electron-donor solvents compared with hydrocarbon solvents must be attributed to the effect of two main factors: the increase of the polarity of the C–Li bond as a result of the specific solvation of lithium and the decrease of the degree of association of the organolithium compound. One should then bear in mind the change of the polarity of the C–Li bond not only in the ground but also in the transition state[4,22,69].

Thus West[47] established the occurrence of a kinetic isotope effect for the reaction between ethyl-lithium and benzyl chloride ($k^6_{LiEt}/k^7_{LiEt} = 1.029$). This finding is evidence of a significant weakening of the C–Li bond in the transition state. Therefore one may expect the acceleration of reactions of this type following the additional polarisation of the C–Li bond, for example, as a result of the solvation of lithium by the molecules of an electron-donor agent.

The increased polarity of the C–Li bond in electron-donor solvents (or when these are added to hydrocarbons) is confirmed by measurements of the infrared spectra[4,6,24,25] electrical conductivity[73], and dielectric constants[10,11] of RLi solutions and also by measurements of their NMR spectra[4,15,26]. On the other hand, as we have seen, in the presence of an electron-donor solvent the degree of association of the lithium alkyl falls and consequently the number of its kinetically active species should increase[22].

The problem of the interrelation of these factors is not entirely clear, although in some studies[22,58,63] the lowering of the degree of association of the organolithium compound is regarded as the most important factor accelerating the reaction. Probably, in each specific case, this problem must be solved separately considering the specific features of the mechanism of the given reaction. In this connection it is appropriate to consider data[21,74] on the effect of tetrahydrofuran (THF) and other electron-donor substances on the kinetics of the reactions of n-butyl-lithium with n-butyl bromide and with triphenylmethane.

The dependence of the rate constant for the first reaction on the content in n-hexane of ethers with 1 and 2 oxygen atoms is shown in Figs. 1*a* and 1*b* and has been explained[21,22] by the active participation in the reaction of the solvates of the association complexes of n-butyl-lithium, the composition and the reactivity of which are determined by the solvation properties of the electron-donor compounds.

The rate of this reaction changes most markedly with increasing ether content when small amounts of it are added to n-hexane: in the region of small molar ratios of the ether and the lithium alkyl (r), ranging from zero to 0.5 for ethyl ether or THF and in the region $r < 1$ for 1,2-diethoxy- and 1,2-dimethoxy-ethane.

Fig. 1 shows that the rate of reaction between n-butyl-lithium and n-butyl bromide continues to increase when ether with one oxygen atom is added also in the region with $r > 0.5$, although more slowly than for $r < 0.5$. The reasons for this increase are discussed in a recent brief communication by Screttas and Eastham[75]. They believe that the effects of the electron-donor solvent on the rate of reaction with participation of the lithium alkyl in the region of r less and greater than 0.5 are fundamentally different. In the region where $r < 0.5$ the ether (or amine) takes part in the solvation of the lithium alkyl and causes the breakdown of its association complexes into dimers [Eqn. (1)].

On the other hand, the increase in the rate of reaction with the concentration of the ether or amine in solution for $r > 0.5$ is attributed[75] to a kinetic, and not thermodynamic, effect of the electron-donor solvent, which facilitates charge transfer from the lithium alkyl to the substrate S, for example:

$$(BuLi)_2.THF + solvent + S \rightarrow [(BuLi)_2.THF]^+_{solvent} + S^- \qquad (12)$$

To describe the kinetic effect of the excess THF or another ether (D) relative to its amount required for the formation of the solvate $(BuLi)_2.D$, the following equation was proposed[75]:

$$V = k([D] - 0.5[RLi])^{\alpha}[RLi]^{\beta}[S]^{\gamma}, \qquad (13)$$

where α, β, and γ are reaction orders with respect to the electron-donor additive, lithium alkyl, and the substrate. Screttas and Eastham[75] applied this equation to their own[22] and certain literature data in order to determine α. In particular they employed the data of Shatenshtein et al,[21] on the kinetics of the reaction of n-butyl-lithium with n-butyl bromide in the presence of added 1,2-dimethoxyethane for $r > 0.5$, although the type of dependence of the rate constants on the content of THF and 1,2-dimethoxyethane is different (cf. Figs. 1*a* and 1*b*). The value of α proved to be close to unity in all cases.

Screttas and Eastham[75] themselves emphasised that their concepts concerning the kinetic role of the electron-donor solvents are extremely hypothetical. Furthermore, Screttas and Eastham evidently continued to hold the view that lithium alkyls are dimerised in ethereal solution. Nevertheless, one should not disregard the possibility of the acceleration of reaction on addition of ether in the region with $r > 0.5$ due to the additional solvation of the association complexes of the lithium alkyl accompanied by the formation, albeit in a small amount, of new reactive complexes of the lithium alkyl with the Lewis base[20,58,74].

We shall now consider how the addition of THF to n-hexane affects the rate of metallation of triphenylmethane by n-butyl-lithium. Fig. 3 shows that, when the concentration of tetrahydrofuran (c_{THF}) is varied from zero to 90 vol.%, the rate constant k increases continuously and the order of the reaction determined from the plot $\lg k$ against $\lg c_{THF}$ (Fig. 4) is approximately 3/2. A detailed study of the region of low THF concentrations (< 2 vol.%) showed that the k–c_{THF} curve makes an intercept on the abscissa axis corresponding to $c_{THF} = 0.36$ vol.% or 0.04–0.05 M. According to the experimental conditions, it corresponds to a molar ratio of the ether and the lithium alkyl of 0.5. This finding can serve as additional confirmation of the hypothesis[21] of the formation of solvate complexes of tetrahydrofuran with n-butyl-lithium, with composition corresponding to the ratio 1 : 2. However, the formation of such primary solvates is probably still insufficient for any significant acceleration of the metallation reaction. Its rate begins to increase only in the presence of an excess of tetrahydrofuran relative to the amount required for the formation of the above solvates.

Waack et al.[58] observed similar behaviour in the study of the effect of small amounts of tetrahydrofuran added to benzene or hexane on the rate of addition of n-butyl-lithium to 1,1-diphenylethylene. Its dependence on the concentration of tetrahydrofuran is very complex. For given proportions of the ether and lithium alkyl, the rate of reaction is greater at higher concentrations of the lithium alkyl. On the other hand, an increase of the concentration of n-butyl-lithium at a constant concentration of the ether entails a decrease of the rate. Waack[58] explained this by

the fact that the lower solvates of n-butyl-lithium are inactive in the reaction.

There arises now the problem of the causes of this marked difference between the effect of tetrahydrofuran on the kinetics of the normal Wurtz reaction and the metallation reaction. The effect of this ether on the kinetics of the metallation of triphenylmethane can be understood, for example, by assuming that the monomeric form of butyl-lithium is active in the reaction, an increase in its content being favoured by the additional solvation of the dimer of the lithium alkyl:

$$(BuLi)_2 \cdot THF \overset{+3THF}{\rightleftharpoons} 2\,[(BuLi) \cdot 2THF]. \qquad (14)$$

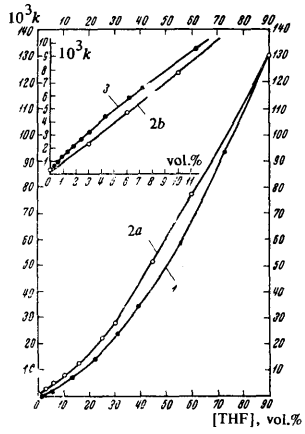

Figure 3. Dependence of the rate constant for the metallation of triphenylmethane with n-butyl-lithium on the content of tetrahydrofuran in n-hexane (*1*) or in ethyl ether (*2a* and *2b*) and on the content in the latter of 1,2-diethoxyethane (*3*).

One cannot exclude the possibility that phenomena involving the solvation of the transition state play a decisive role. Metallation and isotope exchange of hydrogen with bases belong to the same type of protophilic substitution of hydrogen and have similar mechanisms[76]. The transition state in processes of this type has the properties of a carbanion, as shown, in particular, by the determinations of the kinetic isotope effect (KIE) for these and other reactions[77-85].

The determination[74] of KIE (k_H/k_D) for the metallation of triphenylmethane by n-butyl-lithium in tetrahydrofuran, triethylamine, and ethyl ether and also in mixtures of the latter with 1,2-diethoxyethane yielded the same result: $k_H/k_D = 10$ at 25°C, although the rates of reaction in these solvates differed by factors up to 2500.

The relative rate constants (k_{rel}) for the reactions of n-butyl-lithium with n-butyl bromide (I) and triphenylmethane (II) are compared in Table 1. The rate constant for the reaction in the presence of added tetrahydrofuran was assumed to be unity in each case.

There is no correlation between k_{rel} and the polar properties of the solvent, i.e. the dielectric constants (DC) and dipole moments (μ). This is quite reasonable, since the effect of the above solvents on the kinetics of the reactions is due primarily to the specific solvation of the cation, which is of the donor–acceptor type. Furthermore, this hypothesis is not contradicted by the lack of correspondence between k_{rel} and the changes $\Delta\nu_{OD}$ (cm^{-1}) characterising the electron-donor properties of the additives based on the shift of the frequency of the OD bond in deuteriomethanol when the latter forms a hydrogen bond with the heteroatom of the electron donor[17]. The reason for the absence of a parallelism between k and $\Delta\nu_{OD}$ is that the specific solvation processes of alkali metal cations are very sensitive to steric factors[16,20,90,91].

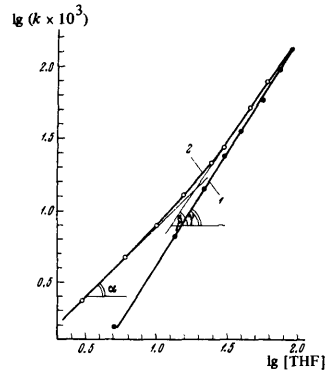

Figure 4. Determination of the reaction order of the metallation of triphenylmethane with n-butyl-lithium from the concentration of tetrahydrofuran in n-hexane (*1*) and in ethyl ether (*2*) (tan $\alpha = 1.0$; tan $\beta = 1.45$; tan $\gamma = 1.6$).

The sequence of the activating effects of the solvents on the reactions of n-butyl-lithium (Table 1) is in the main similar to that observed for other organic reactions of the anionic type[16,92,93]. The higher activity of added tetrahydrofuran and in particular 1,2-dimethoxyethane compared with ethyl ether and triethylamine has also been observed in measurements of the rates of the initiation[61] and chain propagation stages in anionic polymerisation[61,94-96] and also in the analysis of the structure of polydienes and the composition of copolymers[19,61,97-99].

The relative solvating capacity of solvents can also be assessed from the change in the electronic transition energy associated with the principal absorption band in the spectrum of a highly polar organic derivative of an alkali metal[100-102]. In this connection, we may note that the same sequence of solvent effects on the rate of the metallation reaction (Table 1) and on the bathochromic shift in the absorption spectrum of triphenylmethyl-lithium has been observed[74]. The absorption maxima in n-hexane, triethylamine, and ethyl ether are respectively in the region of 420, 430–435, and 435–440 nm. The addition of 11 vol.% of tetrahydrofuran to ethyl ether results in a bathochromic shift of 25 nm and the addition of 11 vol.% of 1,2-diethoxyethane leads to a shift of 55 nm (cf. also Ref. 103).

Attention must be drawn to the following features of the series of relative activities of solvents established for the reactions of lithium alkyls. According to Fig. 3 (curves *2b* and *3*), at low concentrations 1,2-diethoxyethane is more active than tetrahydrofuran but with increase in their content in ethyl ether the order of activity is reversed

(cf. curves *2a* and *3*), i.e. becomes of the type usually observed[16,93,94]. Probably the above concentration dependence is a consequence of different mechanisms of the solvation of the alkali metal by tetrahydrofuran and 1,2-diethoxyethane[16,90,91]. The differences in the solvation of the metal cation by these ethers, which determine their relative activities when the amounts added are small, are obliterated when the ether is used as the solvent. Then other factors, for example, steric considerations become of primary importance. The reversal of the sequence of these ethers is observed also when their effects on the equilibrium formation of diphenylsodium are compared[91] and the reaction itself is carried out in mixtures of either tetrahydrofuran or 1,2-diethoxyethane with n-heptane or when each ether is the solvent.

Relative rate constants for the reaction of n-butyl-lithium with n-butyl bromide (I) for [D]/[n-BuLi] = 1 and with triphenylmethane (II) at 25 °C

Electron-donor additive D	k_{rel} for reaction I[21]	k_{rel} for reaction II[74]	DC(25°) (Ref.86 & 87)	$\Delta\nu$(OD), cm^{-1} (Refs.17 & 18)	μ, D (25°) (Refs.86,88,89)
Diethyl sulphide	0.018	—	5.72	—	—
Triethylamine	—	0.012*	2.42	289	0.77
Ethyl ether	0.6	0.067*	4.33	106	1.15
Tetrahydrofuran	1	1**	7.31	115	1.87
1,2-Diethoxyethane	26	1.25**	4.89	98	1.65
1,2-Dimethoxyethane	52	—	6.96	93	1.72

*90 vol.% of triethylamine or ethyl ether; 10 vol.% of n-hexane.
**5 vol.% of THF or 1,2-diethoxyethane; 85 vol.% of ethyl ether; 10 vol.% of n-hexane.

The study of reactions in mixtures of electron-donor solvents is of interest for the detection of the differences in their solvation properties, since it reveals competitive phenomena between the two solvents in specific solvation processes. Unusual data were obtained in measurements of the rate of anionic polymerisation in mixtures of tetrahydrofuran with 1,4-dioxan[104] and with 1,2-dimethoxyethane[99] and also in the study of the electronic absorption spectra of triphenylmethyl-lithium[74] and 1,1-diphenylhexyl-lithium[102] in mixtures of tetrahydrofuran with aliphatic ethers.

There are still few data on the kinetics of the reactions of lithium alkyls in mixtures of electron-donor solvents. Relations have been established[74] between the rates of metallation of triphenylmethane with n-butyl-lithium and the proportion of 1,2-diethoxyethane or tetrahydrofuran in ethyl ether (Fig. 3, curves *3* and *2a*). The fact that the order of the metallation reaction with respect to tetrahydrofuran changes from unity to 3/2 with increasing concentration of tetrahydrofuran in ethyl ether (Fig. 4), i.e. approaches the order in mixtures of tetrahydrofuran with n-hexane, which is approximately 3/2, may be attributed to competition between the two esters in the lithium solvation processes.

3. The Reactive Forms of Lithium Alkyls in Electron-donor Solvents

In considering the nature of the reactive forms of lithium alkyls in electron-donor solvents one must take into account not only the degree of association and the level and nature of the solvation of the organolithium compound but also the possibility of different states and different degrees of dissociation of the ion pair[16,90,91,105-107]. Bearing this in mind, Ebel[108] suggests the following mechanism for the change in the form of RM in solution and the nature of the bond C–M as a function of the solvent, the nature of the alkali metal M, and the alkyl group R:

$$\overbrace{(RM)_6 \rightleftarrows (RM)_4 \rightleftarrows (RM)_2}^{A} \rightleftarrows \overset{B}{RM} \rightleftarrows \overset{C}{R^-, M^+} \rightleftarrows \overset{D}{R^- \parallel M^+} \rightleftarrows \overset{E}{R^- + M^+}$$

where *A* are association complexes of RM, *B* is a molecule with a covalent bond C–M, *C* and *D* are ion pairs in contact and separated by the solvent, and *E* are free ions. The solvation of the association complexes and ions is not shown in the above mechanism.

As already mentioned, when discussing the kinetics of the reactions of lithium alkyls in the presence of an ether or amine, Scheme 1, (p. 842) is usually employed, i.e. only the monomeric form of the lithium alkyl (*B*) is regarded as reactive[39,58,66,109]. Brown[36] suggests that this is incorrect not only in hydrocarbon but also in electron-donor solvents. Until recently, Brown's hypothesis[4,36] of the possible active participation in the reaction of the association complexes of organolithium compounds was not supported by experimental data if one excludes the results of Eastham and Gibson[15,22] mentioned above (p. 842) (see also Refs. 93, 110, and 111). Brown's conclusions found more definite confirmation in the work of Waack[112], who investigated the kinetics of the metallation of triphenylmethane with phenyl-lithium and the rate of its addition to 1,10-diphenylethylene in tetrahydrofuran. The order of these reactions with respect to phenyl-lithium is 0.65 ± 0.03, i.e. the precision of the determination of the order shows with certainty that it is not unity or 0.5. Analysis of the possible reaction mechanisms and the corresponding reaction orders taking into account the dimeric state of phenyl-lithium in tetrahydrofuran led Waack et al.[112] to the conclusion that both the dimer and monomer of phenyl-lithium participate in the above reactions, the two species being in equilibrium:

$$\frac{1}{2}(PhLi)_2 \overset{K_e}{\rightleftarrows} PhLi\,. \qquad (15)$$

The rate of reaction is given by the equation

$$\frac{V}{[S]} = k_1 K_e \left(\frac{[PhLi]}{2}\right)^{1/2} + k_2 \left(\frac{[PhLi]}{2}\right), \qquad (16)$$

where k_1 and k_2 are respectively the rate constants for the reaction with participation of the monomer and dimer, K_e is the dissociation constant of the dimer, and [S] and [PhLi] are the concentrations of the reactants.

On the basis of these results, Waack[112] arrived at the general conclusion that, depending on the concentration of RLi and the rate constants for the reactions involving the monomer and the association complexes, the reaction order with respect to RLi may vary from 1 to $1/n$, where n is the degree of association of RLi in the given solvent.

The states *D* and *E* (in Ebel's scheme) of the C–M bond, including C–Li, have recently been considered in relation to the active centres of the growing polymeric chains in the study of the kinetics and mechanism of anionic polymerisation in electron-donor solvents. This has been demonstrated particularly clearly in the work of Szwarc and Schulz (see the appropriate reviews[113-115]).

We shall now consider the state of our knowledge concerning the participation of free carbanions in the reactions of lithium alkyls. The electrical conductivity of the hydrocarbon solutions of lithium alkyls is extremely low[63] and remains low even in the presence of electron-donor

additives[73]. Brown[4] admits the possibility that the reaction of RLi takes place partially by a mechanism involving free carbanions in a medium with a high solvating capacity (see Scheme 4, p. 842). However, several attempts[39,63,112] to explain the observed kinetics by the participation of free carbanions of lithium alkyls and even phenyl-lithium have been unsuccessful.

In considering the problem of the reactive forms of lithium alkyls in electron-donor solvents, one must bear in mind that the kinetic effect due to the solvents depends not only on the state of the organolithium compounds in the solutions but also on the mechanisms and other specific features of the reactions.

Summarising, we must emphasise that, although the principal causes of and the relations governing the effect of electron-donor solvents or the corresponding additives on the reactivity of lithium alkyls have been elucidated, some questions, connected with the current problem, still remain controversial.

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Karpov Physicochemical
Institute, Moscow

U.D.C. 547.92

Alkylsteroids

A.A.Akhrem, T.V.Ilyukhina, and Yu.A.Titov

Alkylsteroids constitute an important class of steroid compounds containing additional alkyl groups compared with natural hormones. The introduction of alkyl groups enhances the physiological activity and narrows the spectrum of the biological activity of steroids. Furthermore alkylsteroids are of interest for the stereochemistry of the reactions which take place with participation of condensed alicyclic systems. The methods for the direct introduction of alkyl groups based on the reactions of steroids ketones and epoxides are described.
The bibliography includes 255 references.

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1. INTRODUCTION

One of the principal ways in which the structure of steroids is modified consists in the introduction into the latter of additional alkyl groups (mainly methyl). The alkyl steroids thus produced have in many cases an enhanced physiological activity compared with the initial compound. Even more interesting is the fact that the introduction of alkyl groups alters the relation between different types of physiological activity making it possible to prepare compounds with specific activities. Many alkylsteroids have found application in medical practice—an anabolic preparation dianabol (17α-methyl group), an anti-inflammation agent dexamethasone (16α-methyl group), antiovulatory agents dimethisterone and medroxyprogesterone (6α-methyl group), etc. The effect of methyl groups on certain types of the physiological activity of steroids is described in Table 1.

Table 1. Effect of methyl groups on the physiological activity of steroids (+ increase of activity, − decrease of activity, ± activity unchanged)[2].

Type of activity	Position of methyl group										
	1α	2α	4	6α	7α	9α	11α	16α	16β	17α	21
Androgenic	+	−	−	−	+		−		−	±	
Anabolic	+	−	+	±	+		−			±	
Gestagenic		±	−	+				±	−	+	−
Glucocorticoid	−	+	−	+	−	−	−	+	+	−	±
Mineralocorticoid**	−	+	−	±		−	−	−	−	−	−
Anti-inflammation		+	−	+	−	−	−	+	+	±	+

*Deposition of glycogen in the liver.
**Retention of Na^+ ions.

The study of alkylsteroids has made a considerable contribution both to the stereochemistry of reactions with participation of condensed alicyclic systems and to synthetic organic chemistry. Furthermore, the last available review on alkylsteroids[1] refers to work published up to 1960 and is to a considerable degree obsolete. In view of the large number of studies in which alkylsteroids were synthesised (more than 1500) and the space available, it was necessary to restrict the scope of this review, which includes only the methods for the direct introduction of alkyl groups in reactions with steroid ketones and epoxides. Numerous methods for the indirect synthesis of alkylsteroids in which oxygen- or nitrogen-containing and also unsaturated hydrocarbon substituents are initially introduced into the molecule and then transformed into alkyl groups (formylation and cyanation reactions, reactions with carbenes, Wittig, Mannich, etc. reactions) are not considered in the review. The limits of applicability of various methods for the synthesis of alkylsteroids are shown in Table 2.

Table 2. Different synthetic methods for the preparation of alkylsteroids (according to the data in Sections 2–7).

Method of synthesis	Position of alkyl group introduced															
	1	2	3	4	5	6	7	8	9	10	11	12	15	16	17	20	21
Alkylation of ketones		+		+	+	+	+	+	+			+		+	+		+
Reaction of ketones with organometallic compounds	+	+	+	+		+	+				+	+	+		+	+	
Conjugated addition of Grignard reagents	+			+	+		+		+					+		+	
Reaction of diazomethane with ketones	+			+									+	+	+	+	+
Opening of epoxy-rings by Grignard reagents				+	+	+			+			+	+	+			

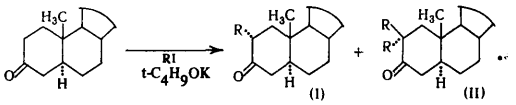
2. ALKYLATION OF STEROID KETONES

In this section two types of alkylation are dealt with—direct alkylation of unsaturated and saturated ketones usually by the action of alkyl iodides in an alkaline medium and reductive alkylation of unsaturated ketones. In the latter case treatment of a conjugated unsaturated ketone with lithium in liquid ammonia yields the enolate which is then treated with alkyl iodide to form the unsaturated alkyl

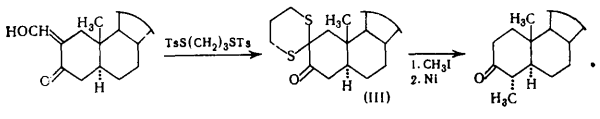
ketone. Methods for the introduction of an alkyl group into α-bromoketones by the simultaneous action of Grignard reagents and alkyl halides and also for the introduction of alkyl groups into unsaturated ketones by treating with alkyl halides the intermediates produced in the conjugated addition of Grignard reagents (see Section 4) resemble this type of alkylation.

The enolic form of the steroid ketone takes part in direct alkylation and therefore the mode of alkylation of the ketone is determined by the mode of its enolisation. Alkaline reaction conditions favour the formation of the most stable isomers. Accordingly 3-oxo-5α,10β- and 3-oxo-5β,10α-steroids are alkylated predominantly at C_2 and 3-oxo-5β,10β- and 3-oxo-5α,10α-steroids[3,4] are alkylated at C_4. 1,3-Diketones are also alkylated at C_2.[5]

The alkylation of 3-oxo-5α-steroids always yields a mixture of 2α-monoalkylsteroids (I) and 2,2-dialkylsteroids (II) the relative amounts of which depend on the reaction conditions. Further alkylation at C_4 either does not occur at all or takes place with a very low yield[6-9]:



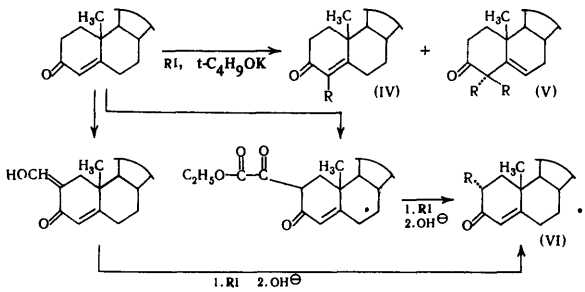
When it is necessary to prepare selectively the 2α-alkylsteroid (I), the formyl or oxalyl derivatives of the initial ketone, which protect it from the introduction of a second group, are alkylated[6,10]. If the desired product is the 4-alkylsteroid, it is necessary to block position 2 completely. One of the possible methods for this consists in the formation of the cyclic thioketal (III) by the reaction of di-*p*-toluenesulphonate of propane-1,3-dithiol with 2-hydroxymethylene derivatives. Subsequent alkylation yields a mixture of 4-methyl derivatives from which the protecting group is readily removed by desulphuration with Raney nickel, the corresponding 4α-methylsteroids being formed[11,13]:



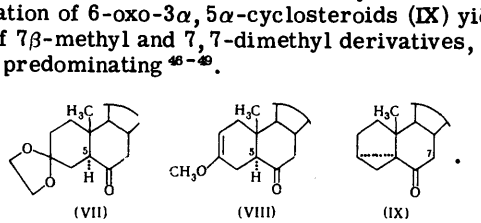
The introduction of a Δ^7-bond into 3-oxo-5α-steroids alters sharply the mode of alkylation towards the formation of 4-methyl derivatives[14-16]. A change of this kind does not take place on introduction of a Δ^6-bond[17] and also in B-norsteroids[18] and Δ^7-5β,10α-steroids[19]; all these compounds are alkylated similarly to the normal series.

The alkylation of 3-oxo-Δ^4-steroids, the products of which usually consist of a mixture of 4-alkyl (IV) and 4,4-dialkyl (V) derivatives, with the latter greatly predominating, has been investigated in greatest detail[6,8,20-25]. Special reaction conditions have been developed for the preferential formation of 4-monoalkylsteroids of type (IV)[26-32]; even under these conditions the presence in the molecule of the initial 3-oxo-Δ^4-steroid of a 6α-methyl group leads to the predominance of dialkyl derivatives in the reaction products[33,34]. It is noteworthy that 3-oxo-$\Delta^{4,7}$-steroids are alkylated similarly to Δ^4-3-ketones, while 3-oxo-$\Delta^{4,6}$-steroids are not alkylated under the usual conditions[35]. This course of reaction was explained by the comparative stability of the conjugated anions corresponding to the successive stages in the alkylation process[36]. The alkylation of 3-oxo-Δ^4-steroids with polymethylene dibromides $Br(CH_2)_nBr$ yields 4,4-spirocycloalkyl derivatives[37].

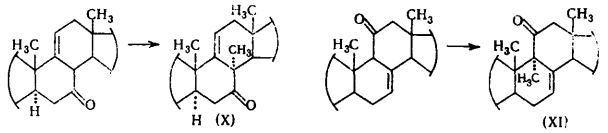
The need to prepare 2-alkyl derivatives of 3-oxo-Δ^4-steroids led to the development of their synthesis via formyl[38,39] and oxalyl[40-43] derivatives. When the primary alkylation product is acted upon by alkalis, the activating groups are hydrolysed with formation of 2α-alkylsteroids (VI).



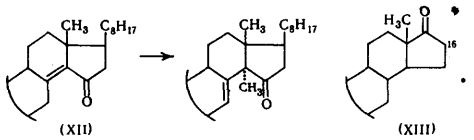
In the alkylation of 6-oxosteroids unsubstituted at C_5 the products are 5-alkyl derivatives the configuration of which depends on the nature of the substituents in the ring A. Thus the ketone (VII) with a dioxolane group forms the corresponding 5β-methyl derivative[44], while the enolic ether (VIII) forms the 5α-methyl derivative[45]. The alkylation of 6-oxo-3α,5α-cyclosteroids (IX) yields a mixture of 7β-methyl and 7,7-dimethyl derivatives, with the latter predominating[46-49].



7-Oxo-Δ^5-steroids are alkylated as a rule at C_6 with formation of dialkyl derivatives[50,51]. However, the introduction of a $\Delta^{9(11)}$-bond into the molecule of a 7-oxosteroid activates the 8-position as a result of which the methylation of these ketones leads to the formation of 8α-methyl derivatives (X)[52,53]. Similarly, 9α-methyl derivatives (XI) were obtained by the methylation of 11-oxo-Δ^7-steroids[54]:

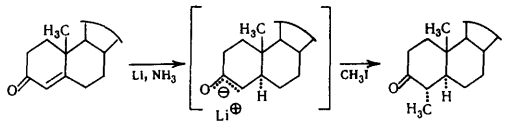


Direct methylation of the 15-oxo-$\Delta^{8(14)}$-steroid (XII) under severe conditions led to the corresponding 14α-methylsteroid with migration of the double bond to the Δ^7-position[24,55,56]. The structural analogues of compound (XII)—A-nor-3-oxosteroids—form on alkylation 5β-methyl derivatives[57]. Both 16α-methyl and 16β-methyl derivatives were obtained from 17-oxosteroids (XIII) under different conditions[29,58,59]:



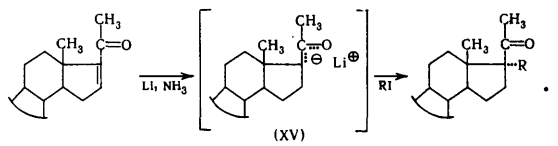
Angular methylation of 18-nor-17-oxo- and 18-nor-17a-oxo-steroids with formation of 13-methyl derivatives is one of the stages in many total syntheses of steroid compounds and has been discussed in detail in a recently published monograph[60].

The so called "reductive alkylation" has found wide application recently in the synthesis of alkylsteroids. For example, when 3-oxo-Δ^4-steroids are acted upon by alkali or alkaline earth metals (lithium, sodium, calcium, or barium) in liquid ammonia, the product is the anion (XIV), the treatment of which *in situ* with methyl iodide gives the 5α-dihydro-4α-methyl derivative[61,62]. When the proportions of the reactants are altered, the 4,4-dimethyl derivative is produced[63]. Similarly, 2α-methyl derivatives were obtained from 3-oxo-$\Delta^{1,4}$-steroids[64] and 4,4-dimethyl-Δ^5-derivatives from 3-oxo-$\Delta^{4,6}$-steroids[61]:



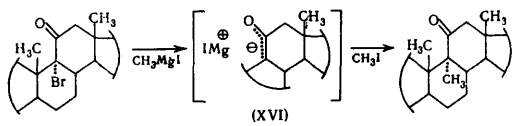
(XIV)

This method of synthesis is employed particularly frequently for the introduction of 17α-alkyl groups into 20-oxo-Δ^{16}-steroids of the pregnane series. 17α-Bromo-, 17α-hydroxy-, and 17α- and 17β-acetoxy-derivatives of 20-oxosteroids, which under the action of lithium and liquid ammonia form the intermediate anion (XV), also enter into this reaction. 17β-Alkyl- and 21-alkyl-steroids are formed in a small amount as side products[56,65-68]:



(XV)

The method for the introduction of alkyl groups into α-bromosteroids by the action of a mixture of a Grignard reagent and a large excess of an alkyl halide has a mechanism similar to that of reductive alkylation. Here the intermediate stage also involves the formation of the enolate anion of type (XV) with loss of a bromine atom; subsequent methylation of compound (XVI) leads to the corresponding 9α-methyl derivative[12,69-71]:



(XVI)

12α-Methylsteroids have been prepared[12] from 12α-bromo-11-ketones by the method described above for the synthesis of 9α-methyl derivatives from 9α-bromo-11-oxosteroids. It proved possible to carry out the same reaction with the enolic acetates of 11-oxo- and 20-oxosteroids, 9α,12β-dimethyl and 17α-methyl derivatives being obtained respectively[70].

3. REACTIONS OF STEROID KETONES WITH ORGANOMETALLIC COMPOUNDS

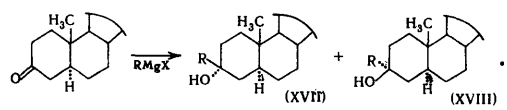
This group of reactions is most widely used for the introduction of alkyl groups into steroid compounds. In recent years it has been shown[72] that ethylene-ketals of 3-, 17-, and 20- oxosteroids also react with Grignard reagents under severe conditions.

A characteristic feature of the reactions of organometallic compounds with oxosteroids is attack from the least sterically hindered side. The stereochemistry of the reaction is influenced by polar groups in the steroid and also by the size and polarity of the attacking agent. The simultaneous effects of all these factors usually lead to the formation of a mixture of reaction products with different steric orientations of the substituted alkyl group[73,74], the isomer with the equatorial alkyl group predominating[74]. Recent studies have shown for 12-, 17-, and 17a-oxosteroids numerous deviations from the so called "rule of attack from the α-side"[75] (opposite to the side of the angular methyl group). Therefore this rule cannot be regarded as having general applicability.

Grignard reactions have been used for the introduction of alkyl substituents into the 1-position[76,77] and the 2-position[78]; in the first case the stereochemistry was not elucidated and in the second only the 2α-alkyl isomer, with an equatorial position of the substituted alkyl group, was obtained.

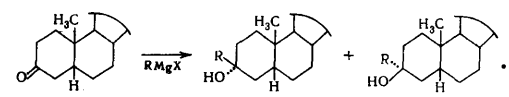
Reactions with participation of 3-oxosteroids have been investigated in incomparably greater detail. Thus in the reaction of 3-oxo-5α-steroids with Grignard reagents a mixture of epimers (XVII) and (XVIII) is usually formed, compound (XVII) with the equatorial 3β-configuration of the substituted alkyl[79-82] or phenyl[83] group [(XVII) : (XVIII) $\simeq$ 1.5–2 : 1)] predominating; in one case the opposite ratio of reaction products was obtained. When the molecule possesses 1α-hydroxy-[84], 1α-methyl-[77], 2α-bromo-[85], and 5α-hydroxy-substituents[86], the reaction of 3-oxo-5-steroids with CH_3MgI and CH_3Li leads exclusively to isomer (XVII) with an equatorial 3β-methyl group. The introduction of a Δ^4-bond into the steroid does not alter significantly the mode of the Grignard reaction: 3-oxo-Δ^4-steroids form approximately equal amounts of 3α- and 3β-alkyl isomers[87], while 3-oxo-Δ^5-steroids yield predominately the 3α-alkyl isomer of type (XVIII)[88].

The Norman reaction with 3-oxo-5α-steroids[81] and ethynylation[74,81,89] involve a stereochemical orientation opposite to that in the Grignard reaction and lead to a mixture of isomers (XVII) and (XVIII), the latter (with an axial alkyl substituent) greatly predominating (1 : 6.5–7.0):



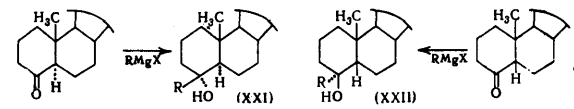
(XVII) (XVIII)

3-Oxo-5β-steroids form in a Grignard reaction mainly the isomer with the axial 3β-configuration of the alkyl group [(XIX) : (XX) = 2 : 1 when R = C_6H_5][90]:



(XIX) (XX)

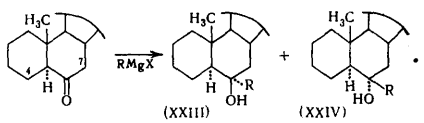
In the Grignard and Iotsich reactions, 4-oxosteroids of the 5α-series yield the axial 4β-alkyl isomer (XXI), while the Iotsich reaction with 4-oxosteroids of the 5β-series results in the formation of the axial 4α-alkyl isomer (XXII)[91-93]:



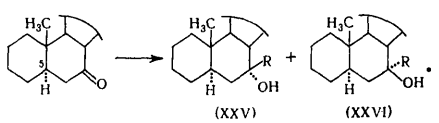
(XXI) (XXII)

6-Oxosteroids form with CH_3MgI only isomer (XXIII) with an equatorial alkyl group[94-98] and introduction of 5α-hydroxy-[99-103] or 7-alkyl[46] substituents does not alter

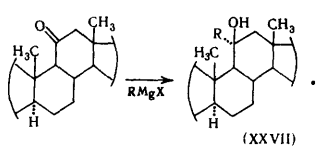
the stereochemistry of the reaction. At the same time in the presence of a 4α-methyl group in the steroid, a 6β-methyl derivative of type (XXIV) was found to predominate [104]. According to some data [105], arylmagnesium bromides form the isomer (XXIII), while according to others [106] the product is the isomer (XXIV). In the Grignard reaction 6-oxo-3α,5α-cyclosteroids form the isomer (XXIV) [107]:



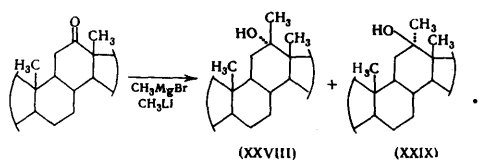
The Grignard reaction with participation of 7-oxo-5α-steroids yields predominately equatorial 7β-alkyl isomers of type (XXV) [108,109]. As with 3-oxosteroids, the introduction of a Δ⁵-bond alters sharply the stereochemistry of the process and isomers of type (XXVI) with an axial methyl group [109,110] at C_7 greatly predominate in the mixture of products of the reaction of 7-oxo-Δ⁵-steroids with CH_3MgI and CH_3Li:



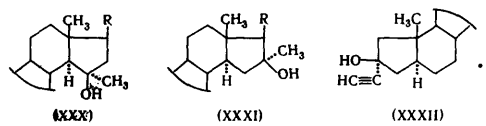
The sterically hindered 11-oxo-group is nevertheless susceptible to attack by organometallic compounds. Only the equatorial 11-alkyl derivatives of type (XXVII) were observed in all cases; methyl-lithium and the Iotsich agent form this product in higher yields than methylmagnesium bromide [111-117]. The reaction is more difficult with 11-ketones of the 5β-series and also in the presence in the steroid molecule of a free 17α-hydroxy-group; in both cases the approach of the reactant from the α-side of the steroid molecule is sterically hindered [112,118,119]:



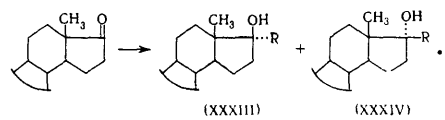
Despite earlier data [120,121], 12-oxosteroids form with organometallic compounds a mixture of isomers (XXVIII) and (XXIX) in which the equatorial 12β-methyl derivative (XXVIII), formed as a result of attack from the β-side of the steroid molecule [122-125], predominates:



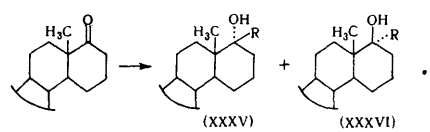
The reaction of 15-oxosteroids of the pregnane series with methylmagnesium bromide yields the 15α-methyl derivative (XXX) [126]. Both in the presence and absence of a 17β-hydroxy-group, 16-oxosteroids form with methylmagnesium bromide [127,128] and ethynyl-lithium [129,130] only 16α-alkyl derivatives of type (XXXI). The C_{16} position is stereochemically equivalent to the C_2 position in A-norsteroids. Therefore 2-oxo-A-norandrostanes react with ethynyl-lithium, forming a mixture of isomers in which the 2α-ethynyl derivative (XXXII) greatly predominates [131,132]:



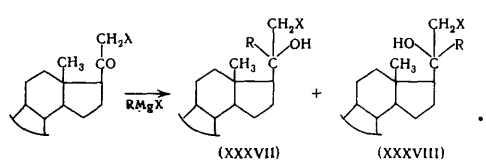
In the reaction of organometallic compounds with 17-oxosteroids, the products are mainly 17α-alkyl derivatives of type (XXXIII) [133]. The stereochemistry of the reaction does not alter when the molecule contains 16α-methyl and 16-spirocyclopropyl groups [29,134,135]. The reaction with methyl-lithium gives higher yields and is more stereospecific than the reactions with Grignard reagents [136,137]. In a number of studies small amounts of the 17β-alkyl isomer (XXXIV) were detected in the mixture of products of reactions of 17-oxosteroids with methyl [138], phenyl [139], and allyl [139,140] Grignard reagents. The isomer (XXXIV) predominates when the 17-oxosteroid molecule contains 12β-hydroxy- [141], 16α-acetoxy- [127], and 16α-fluoro-substituents [142] and also in the reaction of the methyl ether of oestrone with $KC{\equiv}CCH(OC_2H_5)_2$ (the potassium derivative of the diethylacetal of propiolic aldehyde) [143]:



The reaction of 17α-oxo-derivatives of D-homosteroids with organometallic compounds yields a mixture of isomers, the composition of which depends on the reagent employed. Grignard reagents form mainly the isomer (XXXV), corresponding to the equatorial substitution of an alkyl group, while methyl- and ethynyl-lithium give rise to a mixture of products in which the isomer (XXXVI) with an axial methyl (ethynyl) group predominates [144-149]:



A product with the 19-S-configuration is formed in the reaction of steroid 19-aldehydes with methyl-lithium [150]. 20-Oxosteroids unsubstituted at C_{21} react with methylmagnesium iodide, forming almost exclusively the 20β-methyl derivative (XXXVII) [151]. The 21-acetoxy-derivative (X = OAc) forms a mixture of isomers containing up to one-third of the 20α-alkyl derivative (XXXVIII) [152]:

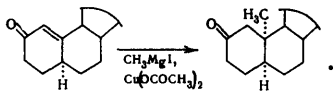


4. CONJUGATED ADDITION OF GRIGNARD REAGENTS TO UNSATURATED STEROID KETONES

In 1941 it was shown [153] that in the presence of copper(I) salts Grignard reagents add to αβ-unsaturated ketones in the 1,4-position forming β-alkyl ketones. The mechanism of this addition is probably similar to that of the Michael reaction but, in contrast to the latter, conjugated addition

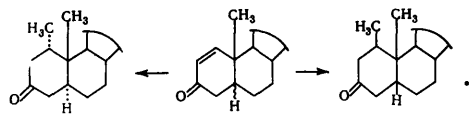
is an irreversible reaction[154]. A special review has been devoted[155] to the stereochemistry of conjugated addition involving cyclic $\alpha\beta$-unsaturated ketones.

Several types of steroid structures allowing the conjugated addition of Grignard reagents have been described. Thus 2-oxo-$\Delta^{1(10)}$-steroids combine with methylmagnesium iodide to form 10α-methylsteroids (XXXIV)[156,157]:



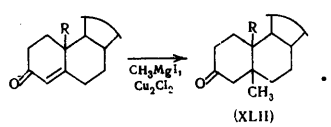
(XXXIX)

The reaction of a Grignard reagent with 3-oxo-Δ^1-steroids of the 5α-series yields the 1α-methyl derivatives (XL)[158-161], while the 1β-methyl derivatives (XLI) are formed from the 5β-analogues[162-164]:



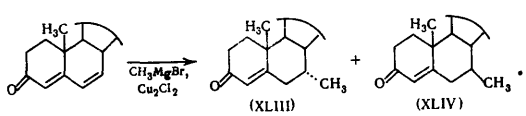
(XL) (XLI)

3-Oxo-Δ^4-steroids usually react with Grignard reagents by a mechanism involving 1,2-addition even in the presence of copper salts[165]. Only with testosterone was it possible to obtain a low yield of the 5β-methyl derivative (XLII; R = CH_3)[166]. Much higher yields (60–80%) were obtained with 19-norsteroids (R = H) where the absence of a methyl group at C_{10} considerably reduces the steric hindrance to the approach of the bulky Grignard reagent[165,166]:



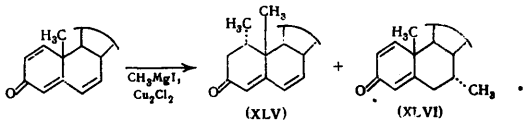
(XLII)

Conjugated 3-oxo-$\Delta^{4,6}$-steroids combine with methylmagnesium bromide in the 1,6-position with formation of 7α-methyl derivatives (XLIII)[29,167]; however, when the steroid contains an 11β-hydroxy-group, a mixture of 7α- and 7β-methyl derivatives is formed, with the 7β-isomer (XLIV) predominating[168]:



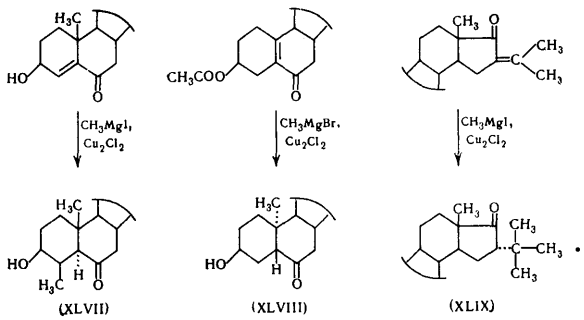
(XLIII) (XLIV)

The addition of Grignard reagents to 3-oxo-$\Delta^{1,4,6}$-steroids takes place in one or other conjugated system depending on the structure of the steroid and either the 1α-methyl derivative (XLV) or the 7α-methyl derivative (XLVI) predominates in the reaction products, with a small admixture of 1α,7α-dimethyl derivatives[169,170]:



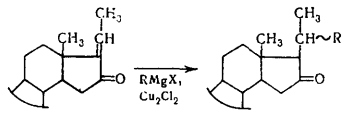
(XLV) (XLVI)

6-Oxo-Δ^4-steroids[171] and 6-oxo-$\Delta^{5(10)}$-steroids[172] form with Grignard reagents 4β-methyl (XLVII) and 10α-methyl (XLVIII) derivatives respectively. The reaction of 16-isopropylidene-17-oxosteroids yields the 16α-t-butyl derivative (XLIX)[78]:



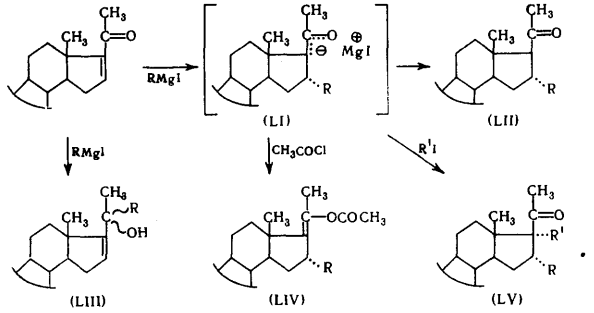
(XLVII) (XLVIII) (XLIX)

16-Oxo-$\Delta^{17(20)}$-steroids react with Grignard reagents to form a mixture of approximately equal amounts of 20α-alkyl- and 20β-alkyl-steroids (L)[173]:



(L)

The conjugated addition of Grignard reagents to 20-oxo-Δ^{16}-steroids has been investigated in greatest detail. Without added copper salts, products of both 1,2-addition [compound (LIII)] and 1,4-addition [compound (LIV)] are formed, the fraction of the latter increasing with the size of the alkyl radical R.[174] The addition of copper salts displaces the reaction almost entirely towards 1,4-addition with formation of 16α-alkylsteroids (LII)[175-182]. Structural changes in rings A and B have hardly any effect on the yield of compound (LII) but the presence of a 21-hydroxy-group lowers it significantly[183]. The presence of a 16-methyl group in the initial 20-oxo-Δ^{16}-steroids does not preclude high yields of 16,16-dimethyl derivatives[184,185]. Treatment of the intermediate enolate (LI) with acetyl chloride yields the enol acetate (LIV) which constitutes the starting material for the synthesis of 17α-hydroxysteroids[183,186] and treatment of compound (LI) with alkyl halides gives 16α,17α-dialkylsteroids (LV)[187]. All these findings greatly extend the scope of the synthetic applications of the conjugated addition reactions of Grignard reagents.



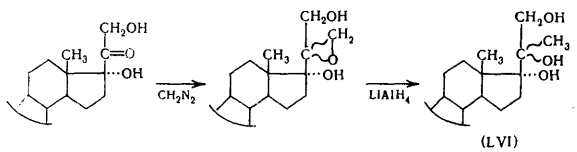
(LI) (LII) (LIII) (LIV) (LV)

5. ADDITION OF DIAZOMETHANE TO STEROID KETONES

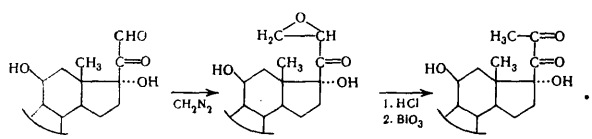
Diazomethane can react with carbonyl-containing steroids in two ways. Either by addition to the carbonyl group with formation of an epoxide or by addition to the

C=C double bond adjacent to the oxo-group with formation of pyrazoline †. The cleavage of the primary addition products leads to the formation of alkylated homologues of steroids.

The first addition mechanism obtains in reactions of diazomethane with 20-ketones [188] and 21-aldehydes [189,190] of the steroid series. The epoxides formed, containing one carbon atom more than the initial compounds, serve as the starting material for the synthesis of 20-methylsteroids (LVI) and 21-methylsteroids (LVII):

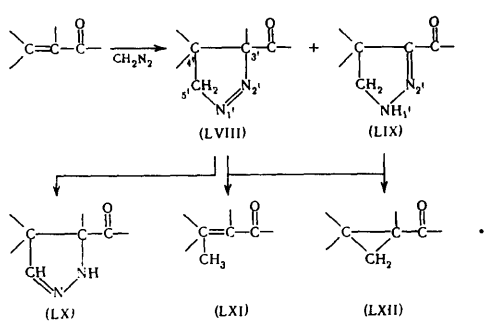


(LVI)



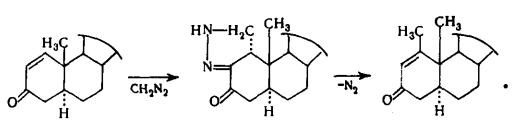
(LVII)

Diazomethane adds to the double bond of $\alpha\beta$-unsaturated ketones with formation of $\Delta^{1'}$-pyrazolines (LVIII) or the isomeric $\Delta^{2'}$-pyrazolines (LIX). Pyrolysis, photolysis, or acidolysis of these pyrazolines can lead to two main products—the methyl ketone (LXI) or the cyclopropyl ketone (LXII)—depending on the reaction conditions and the position of the pyrazoline group in relation to the steroid skeleton. For $\Delta^{1'}$-pyrazoline (LVIII), the possibility of isomerisation to the more stable $\Delta^{5'}$-pyrazoline (LX) has also been noted [39,191,192].



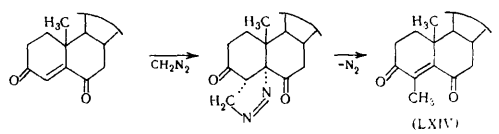
(LVIII) (LIX) (LX) (LXI) (LXII)

In the reaction of 3-oxo-Δ^1-steroids with diazomethane the product is a pyrazoline derivative which on heating or on contact with an acid adsorbent splits off nitrogen forming the 1-methylsteroid (LXIII) as the main reaction product [77,160,193,194]. 3-Oxo-$\Delta^{1,4,6}$-steroids react with diazomethane similarly, forming products of the addition to the Δ^1-bond adjacent to the oxo-group [160,194]:

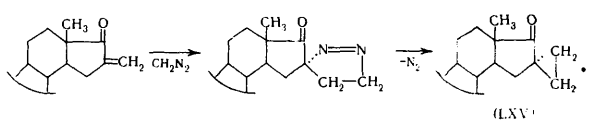


(LXIII)

The products of the addition of diazomethane to 3,6-dioxo-Δ^4-steroids form the 4-methyl derivative (LXIV) on pyrolysis and a mixture of equal amounts of compound (LXIV) and the corresponding $4\alpha,5\alpha$-cyclopropyl derivatives on photolysis [195,196]. At the same time the pyrazoline derivatives obtained from the 16-methylene-17-oxosteroids form 16-spirocyclopropylsteroids (LXV) as the sole product both in pyrolysis and in the reaction with BF_3 in acetone [135]:

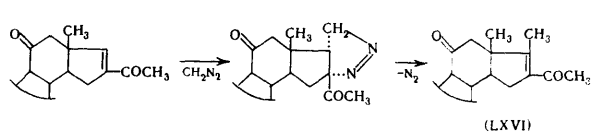


(LXIV)

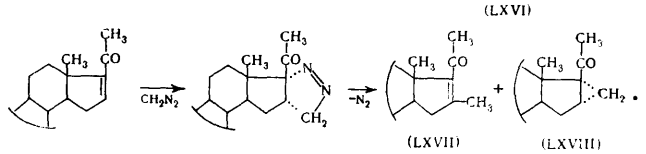


(LXV)

The reaction of 16-acetyl-Δ^{16}-steroids with diazomethane and subsequent pyrolysis yield the 17-methyl derivative (LXVI) [197], while the isomeric 20-oxo-Δ^{16}-steroid can serve as the starting material for the synthesis of 16-methyl derivatives of type (LXVII). Pyrolysis of the intermediate pyrazoline derivative gives predominantly compound (LXVII) and photolysis and acidolysis yield the $16\alpha,17\alpha$-methylenesteroid (LXVIII) [194,196,198-203]. Compounds of type (LXVIII) were also obtained in the reaction of 20-oxo-Δ^{16}-steroids with diazoethane [39] and the diazoacetic ester [204]; at the same time Δ^{16}-etianic acids form 16-methyl derivatives of type (LXVII) [205]:



(LXVI)



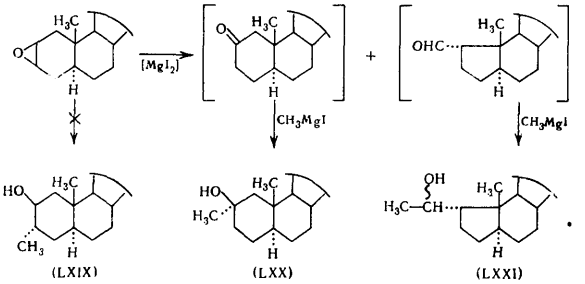
(LXVII) (LXVIII)

6. OPENING OF STEROID EPOXIDE RINGS BY GRIGNARD REAGENTS

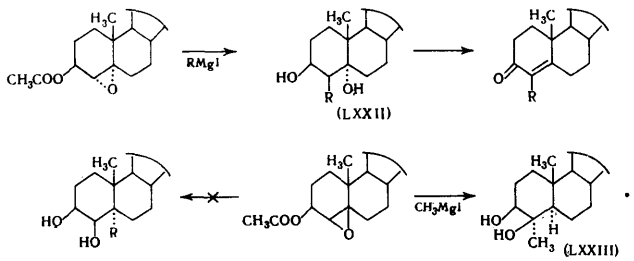
The opening of steroid epoxide rings by Grignard reagents was achieved for the first time in 1939 by Ushakov and Madaeva [206,207]. This reaction is carried out under severe conditions—refluxing in tetrahydrofuran (THF) or a mixture of ether and benzene using a large excess of the Grignard reagent. Therefore, apart from the main ring-opening reaction, various types of rearrangement also take place, due to the effect of magnesium halide in the Grignard reagent [208,209]. Thus in the reaction of the $2\beta,3\beta$-epoxide of the cholestane series with methylmagnesium iodide, a mixture of compounds (LXX) and (LXXI) was obtained instead of the expected ring-opening product (LXIX) [210]. These compounds are formed as a result of the attack of the Grignard reagent on the corresponding ketone and A-noraldehyde, which are the isomerisation products of the initial $2\beta,3\beta$-epoxide. Similar rearrangements also occur in Grignard reactions with participation of steroid 3α-acetoxy-$4\alpha,5\alpha$-epoxides [86,211], 3β-acetoxy-$4\beta,5\beta$-epoxides [212], 3β-acetoxy-$5\beta,6\beta$-epoxides [213], and $11\beta,12\beta$-epoxides. [214]; in the last case rearrangement can be avoided by using

† The ring expansion in reactions of diazomethane with steroid ketones is not discussed in this review.

dimethylmagnesium instead of methylmagnesium 10-dide[214,215].

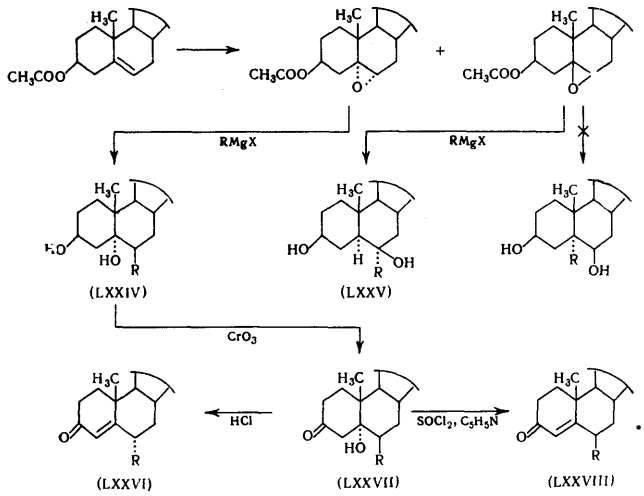


Normal ring opening of the epoxides of the steroid series by Grignard reagents results in the formation of *trans*-diaxial products. For example, the reaction of 3β-acetoxy-4α,5α-epoxide with Grignard, Norman, and Iotsich reagents yields 4β-alkyl(vinyl, ethynyl)-5α-hydroxy-derivatives (LXXII)[216-221]. The presence of a methyl group in the 6α-position does not alter the stereochemistry of the ring-opening reaction[33,222]. By oxidising compounds of type (LXXII) and subsequent dehydration, the corresponding 4-alkyl-3-oxo-Δ⁴-steroids were obtained. Despite earlier data[223], 3β-acetoxy-4β,5β-epoxides do not give rise to normal ring-opening products under the action of Grignard reagents; under these conditions, compound (LXXIII), formed as a result of the rearrangement of the epoxide ring to the 4-ketone and the attack of methylmagnesium iodide on this compound, was isolated[212]:

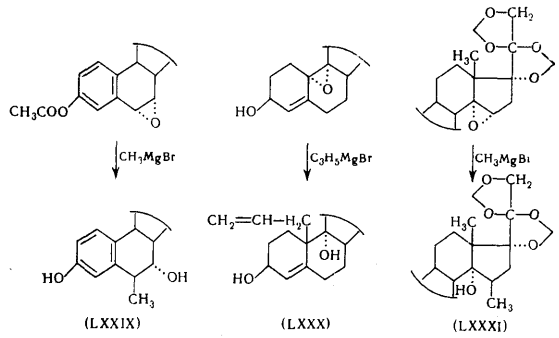


The introduction of epoxy-groups into Δ⁵-steroids leads as a rule to a mixture of both epimeric 5,6-epoxides, in which the 5α,6α-isomer greatly predominates. The opening of the epoxy-ring in the latter under the influence of Grignard reagents yields the 6β-alkyl-5α-hydroxy-derivative (LXXIV)[180,224-232]. Despite earlier data[233], the Grignard reaction involving 5β,6β-epoxides is anomalous. In the first stage the epoxy-ring isomerises with formation of a 6-oxosteroid, which, on being attacked by Grignard reagents, gives rise ultimately to the 6β-hydroxy-6α-methyl derivative (LXXV)[234].

Compounds of type (LXXIV) are converted into the corresponding physiologically active 6-alkyl-3-oxo-Δ⁴-steroids by various methods, depending on the structure of the initial compounds. Oppenauer oxidation or oxidation with CrO_3 of the 3-hydroxy-group yields the 3-oxosteroid (LXXVII), the dehydration of which under acid conditions is accompanied by the inversion of the 6β-alkyl group and the formation of the 6α-alkyl steroid (LXXVI). When the 6β-alkylsteroid (LXXVIII) is required, the dehydration is carried out under neutral or weakly alkaline conditions[29,177,178,235-242].

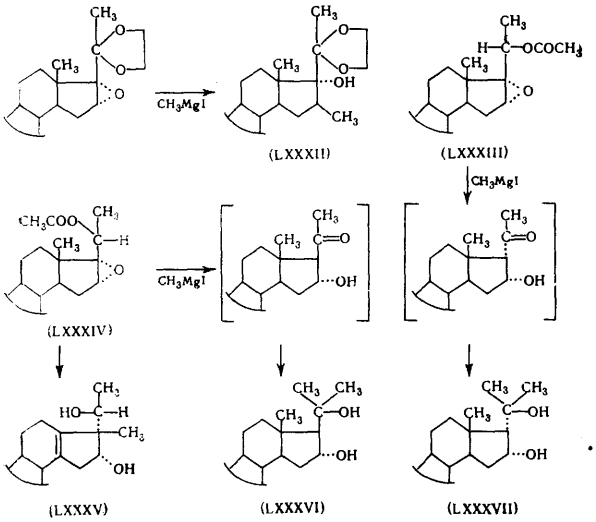


By opening the epoxy-ring of the 6α,7α-epoxide of the oestrane series, the 7α-hydroxy-6β-methyl derivative (LXXIX) was obtained[243]. The 9α,10α-epoxide produced by total synthesis forms the normal epoxy-ring opening product (LXXX) with allylmagnesium bromide; it is interesting to note that this reaction does not take place with Grignard reagents containing saturated alkyl radicals[244]. The reaction of the 14α,15α-epoxide with methylmagnesium bromide yielded the 14-hydroxy-15β-methylsteroid (LXXXI)[245]:



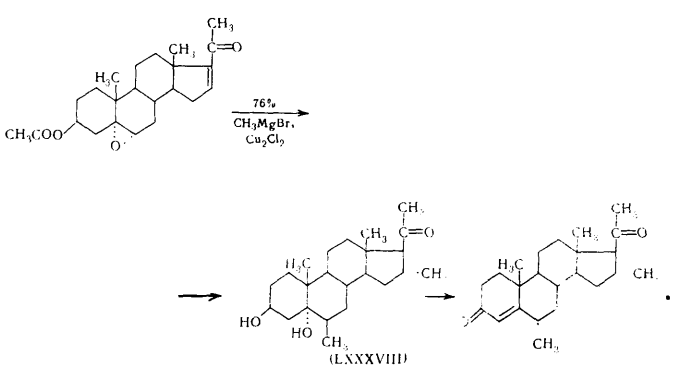
The Grignard reaction of the 20-ethyleneketal of the 16α,17α-epoxy-20-oxosteroid involves the opening of the epoxy-ring and the formation of the 17α-hydroxy-16β-methyl derivative (LXXXII)[246-248]. The Grignard reactions of epimeric 20-acetoxy-16α,17α-epoxysteroids are unusual. Apart from undergoing the Wagner–Meerwein rearrangement to compound (LXXXV), the acetoxy-derivative (LXXXIV) also isomerises to the corresponding 16α-hydroxy-20-ketone which reacts further with the Grignard reagent to form the 20-methylsteroid (LXXXVI). Under the action of the Grignard reagent, the epimeric 20α-acetate (LXXXIII) forms the 20-methyl steroid (LXXXVII) with the 17α-configuration of the side chain, which suggests the

intermediate formation of the 16α-hydroxy-17α,20-oxo-compound[249-254].



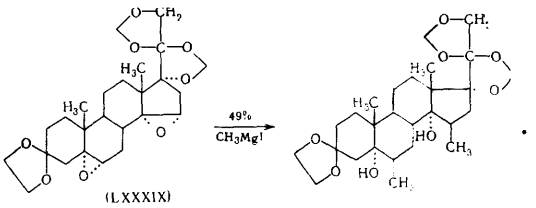
7. SIMULTANEOUS INTRODUCTION OF TWO ALKYL SUBSTITUENTS

The application of the methods discussed in Sections 2–6 to bifunctional steroid derivatives permits the introduction of two alkyl groups in a single stage. An example of this is provided by the reaction of methylmagnesium bromide with the epoxide of hydroxydehydropregnenone in which the epoxy-ring is opened with the introduction of a 6-methyl group and there is conjugated addition to the αβ-unsaturated ketone with the introduction of a 16-methyl group. The product (LXXXVIII) serves as the starting material for the synthesis of 6α, 16α- and 6β, 16α-dimethylsteroids[177,178,182,186]:



The synthesis of compound (LXXXVIII) is an example of reactions with two different functional groups. Other examples of this kind are provided by Grignard reactions with 3,17-dioxo-Δ[1]-steroids[160] and 6,20-dioxo-Δ[16]-steroids[177,182] where dialkyl steroids are formed as a result of 1,2-addition to one of the oxo-groups and conjugated 1,4-addition to the unsaturated group incorporating the second oxo-group.

Dialkylsteroids can also be obtained by the action of organometallic compounds on steroids with two similar reactive groups. Thus, following ring opening under the action of methylmagnesium bromide, the 5α,6α; 14α,15α-diepoxide (LXXXIX) forms the 6,15-dialkyl derivatives[245]:



Two alkyl groups are introduced in the corresponding positions of the steroid skeleton under the action of Grignard reagents on 3,17-dioxo-[82] and 11,17-dioxo-steroids[111]; dialkyl derivatives are also formed as side products form 7,11-dioxosteroids[255]. When an attempt was made to introduce simultaneously two methyl groups by a Grignard reaction with 6,17-diketones, individual products could not be isolated[94].

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Zelinskii Institute of Organic Chemistry,
USSR Academy of Sciences, Moscow

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Condensed Phosphates in the Molten State

N.K.Voskresenskaya and I.D.Sokolova

Problems of the determination of the anionic composition of melts of condensed phosphates and the application of the "theory of the disordered reorganisation of condensed polymers" (Flory, Van Wazer) to them are considered. The part played by water in the formation and breakdown of polymeric chains and rings is noted. The liquidus diagrams of systems based on condensed phosphates of various anionic compositions are reviewed and compounds formed in the system are noted. The physical properties of phosphate melts (mainly surface tension, density, and their temperature coefficients) and their dependence on the type of equilibrium diagram, melt composition, and generalised moments of the cations and anions are examined. It is concluded that the interparticle interaction of polyphosphates in the liquid phase is reflected in their volume and surface properties. 157 references.

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I. INTRODUCTION

Melts of condensed phosphates are attracting attention not only for themselves but also as a comparatively easily investigated model of an inorganic polymer, especially of silicate melts. They are of interest to various branches of learning and technology: nuclear physics, fertiliser technology, metals, electrometallurgy, etc. Crystalline and vitreous substances with valuable physical properties are obtained from the melts. There has recently been an increasing number of papers on condensed phosphate melts. However, Van Wazer's monograph[1] and Thilo's review papers[2,3] did not devote much space to the properties of melts, what was said being distributed in various sections. It is interesting to systematise the available information in terms of physicochemical analysis.

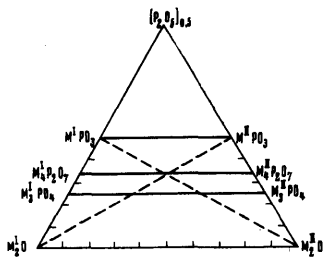

Figure 1. Composition triangle of the $M_2^{I}O-P_2O_5-M_2^{II}O$ system, where M is an equivalent of a metal.

Condensed phosphates are compounds in systems formed by phosphorus pentoxide with oxides of one or two metals; instead of one of the oxides they may contain water. The compositions are characterised by the ratio $R = M/P$, where M is the number of equivalents of the metal and P the number of phosphorus atoms. In the condensed phosphates PO_4 tetrahedra are connected through oxygen atoms with the formation of rings, chains, or networks. Although representatives of this class of compound were known at the start of the last century the study of the condensed phosphates became systematic only after the main feature of their structure as polymers was established. We will be interested in the part of the system (Fig. 1) corresponding to compositions with $R \geqslant 1$, not containing hydrogen. In Fig. 1 this part of the system is represented by the trapezium $M^{I}PO_3-M^{II}PO_3-M^{II}O-M_2^{I}O$. The compounds corresponding to this region are obtained by the thermal dehydration of acid phosphates or their mixtures with oxides or carbonates.

Compositions with $R = 1$ are termed "proper" metaphosphates, or simply metaphosphates. Their general formula is $(MPO_3)_n$, where $n = 3-8$.[2,4,5] They all have a ring structure. Condensed phosphates with $R > 1$ correspond to the general formula $(MPO_3)_n \cdot M_2O$ or $M_{n+2}P_nO_{3n+1}$ and have a chain structure. They are termed polyphosphates. Polyphosphates are the main constituent of melts. The initial member of the series of polyphosphates with very large values of n, that is, with a ratio R which is very little in excess of unity, is usually called metaphosphate, as are the ring phosphates. To distinguish the chain phosphates (with large n) from the ring phosphates with the same number of phosphorus atoms in the formula the word "meta" is inserted in the name when we are dealing with a ring phosphate, or the word "poly" when we are dealing with a chain; however, the word "poly" is sometimes omitted. Hence names such as "tetrametaphosphate" and "tetraphosphate" are obtained; the latter would be more accurately named a tetrapolyphosphate. The final term of the polyphosphate series ($R = 3$) is a compound with one PO_4 group, a monophosphate, better known under the name of orthophosphate; the penultimate term of the series ($R = 2$) is a di- or pyro-phosphate. In the polyphosphates where n is large two equivalents of metal are evidently replaced by hydrogen atoms which enter into the terminal groups with formation of hydroxyl groups. Hence the formula of the long-chain polyphosphates is more accurately written as $M_nH_2P_nO_{3n+1}$. †

† As lattice polyphosphates are almost absent from melts[6] we will not discuss their structure.

Some investigators do not take into account the hydrogen in the terminal groups and the polyphosphates are represented by formulae $M_{n+2}P_nO_{3n+1}$. These formulae are unconditionally applied to polyphosphates with n not exceeding 8–10, which are called oligophosphates[7].

II. ANIONIC COMPOSITION OF THE MELTS

The anionic composition of phosphate melts is determined predominantly by investigating the glasses into which melts of many phosphates with $R < 2$ (that is, in the metaphosphate–diphosphate region) are readily converted. There is a possibility of bringing phosphate glasses into solution without change in anionic composition by the choice of appropriate solvents or by double decomposition with salts and complexones and also with the aid of ion-exchange resins. The anionic composition of the solutions obtained can be determined by chemical analysis[8], by the method of titration of terminal groups[9,10], and by the methods which are general for polymer physics: ultracentrifugation, dialysis, electrophoresis, light scattering studies, viscosity of dilute solutions in the presence of an indifferent electrolyte, etc. However, the greatest possibility was revealed by paper chromatography, applied to polyphosphates by Ebel[11], subsequently perfected and now widely used.

The identity of the structural units of melts and of glasses has been shown by several investigators[12-18] using Raman and infrared absorption spectra, unfortunately for not many compositions. These results showed that in glasses there are chain and a few ring phosphates, and that branching is almost absent. The anions were identified on the basis of a comparison of the spectra of glasses and melts with the spectra of crystals of individual phosphates the structure of which had been found by X-ray diffraction or other methods.

Chromatographic investigation of phosphate glasses was undertaken from the 1950's onwards over the widest front by the schools of Thilo[19-21], Van Wazer and Westmann[22-31], and Meadowcroft and coworkers[32]. In the fusion of even definite crystalline phosphates—tri- and tetra- (but not di-) phosphates—a mixture of anions is formed, in which an anion with a chain length one unit less than the mean chain length ($\bar{n}$) predominates; the mean chain length is easily related to the relative concentration of the oxides $R = M/P$ by the ratio $\bar{n} = 2/(R-1)$. The isolated PO_4^{3-} ion was observed only in melts with $n < 2$, that is, in melts of mixtures of diphosphate and orthophosphate (see Ref. 1, p. 477).

The investigation of the anionic composition of the glasses does not give any idea of the state of the melts, since in the latter, their viscosity being low in comparison with that of glasses, processes connected with the formation of radicals and reactions with participation of the latter are possible. According to some investigators[21,33], many conversions in polyphosphate melts are connected with the formation of intermediate products—the radicals $NaPO_3$, PO_3, etc.

A guideline in ideas about the anionic composition in melts of chain polymers was given by the application to phosphates of the "theory of the disordered reorganisation of condensed polymers", Flory[34] having investigated the polymerisation of organic liquids. He considered the statistical polymerisation of hydroxy-acids, by assuming exchange between the molecular constituents of their "segments". These concepts and methods were transferred by Van Wazer[1,35,36] to polyphosphates. A phosphate melt with a definite value of n is characterised by the retention of some unchanged number of terminal phosphate groups PO_4^{2-}

and of intermediate PO_4^- groups:

analogous to the "segments" of Flory. Van Wazer finally obtained the distribution function—an equation for the determination of the anionic composition with a specified mean chain length $\bar{n}$. If the electrolytic dissociation in the melt were high then the anionic chains would behave as "rigid rods", owing to the high concentration of negative charges; if the dissociation were small then the negative charges would be partly neutralised and the anions would behave as "flexible chains". In the absence of PO_4^{3-} ions and of unreacted oxides the distribution function, which characterises the weight distribution of phosphorus along chains of different length, at a mean chain length of $\bar{n}$ for "flexible chains" will have the form:

$$\omega_{(n)} = \frac{n}{n(n-1)} \left(\frac{n-2}{n-1}\right)^{n-2} \qquad (1)$$

where $\omega_{(n)}$ is the weight fraction of the phosphorus in chains containing n phosphorus atoms; $n \geqslant 2$. For "rigid rods" the distribution function becomes more complex. In some papers[26,28,32] the experimental and theoretical conclusions about the distribution of phosphorus along chains of different length have been compared for glasses of various compositions. The results of chromatographic experiment were treated theoretically on the basis of equations following the Flory theory. The experimental results lie between the calculated ones obtained assuming "flexible chains" and "rigid rods". In recent years the theory has been developed further[37,38]. However, the most significant conclusions yet were derived from Flory's original theory.

Meadowcroft and Richardson[32] attempted to arrive at the thermodynamic properties of polyphosphate melts by using Flory's theory, the equations of which acquired a form convenient for thermodynamic evaluation. The Flory distribution formula is represented in the form:

$$N_n = \left(\frac{\bar{n}-1}{\bar{n}}\right)^{n-1} \cdot \frac{1}{\bar{n}} \qquad (2)$$

where N_n is the mole fraction of the n-mer in the mixture, and $\bar{n}$ is the mean chain length. Each n-mer is in equilibrium with decomposition products:

$$2P_n = P_{n-1} + P_{n+1} \,. \qquad (3)$$

The equilibrium constant (K) of the reaction is given by

$$\frac{[P_{n-1}] \cdot [P_{n+1}]}{[P_n]^2} = K_n \,. \qquad (4)$$

The expressions in square brackets denote the mole fractions of each polymer. The $(n-1)$-mer and $(n+1)$-mer obtained also disproportionate:

$$2P_{n-1} = P_{n-2} + P_n \qquad (4a)$$

$$2P_{n+1} = P_n + P_{n+2} \text{ etc.} \qquad (4b)$$

Each of the equations is characterised by a definite equilibrium constant. When all the other mole fractions of the polymers remaining for the equilibrium constants from

Eqn. (2) are substituted in Eqn. (4) we find that all the constants are equal to unity. It was found[32] that the experimental values of the constants obtained by chromatography of a series of partitions ($n = 4$, 6; cations Na^+, Li^+, Ca^{2+}, Zn^{2+}) are not unity; this shows that the distribution of phosphate along chains of different length is not completely disordered. With increase in n the constants approach 1 and (in some instances) even exceed 1. The departure from 1 at the same mean chain length $\bar{n}$ decreases in the order Na–Li–Ca–Zn.

In the expression:

$$RT \ln K_n = \Delta G_n = \Delta H_n - T\Delta S_n \qquad (5)$$

Meadowcroft and Richardson[32] neglected the entropy term, for doing which there is some justification, since the disproportionating anion is extremely similar to those which are formed. From K_n they found ΔH_n, the heat of disproportionation, which was positive, that is, the process is accompanied by absorption of heat. For a given cation ΔH_n increases as $\bar{n}$ is reduced, that is, as the chain is shortened. This is understandable, since the less $\bar{n}$, the greater the difference between the neighbour n-mers. At a given value of $\bar{n}$ the heats of disproportionation decrease in the order K(Na)–Li–Ca–Zn. Since in the expression

$$d \ln K_n / dT = \Delta H_n / RT^2 \qquad (6)$$

ΔH_n is small, it follows that the temperature change of the anionic composition is insignificant. As experiment shows, it is almost undetectable with the present accuracy of partition chromatographic analysis of glasses.

III. WATER IN PHOSPHATE MELTS

In the formation and changes of condensed phosphates water plays a large part, since as noted above there are hydroxide ions in the terminal groups of long-chain phosphates. The participation of water has been best studied for sodium phosphates. During the dehydration of the dihydrogen phosphate at ~ 240°C in addition to trimetaphosphate chain polyphosphates are formed (crystalline Madrell's salt) and above 400°C these are completely converted into crystals of a cyclic trimetaphosphate[39], the chain closing into a ring with the release of water from the terminal groups. It partly volatilises and partly remains, possibly even forming clathrates. During fusion a large part of the trimetaphosphate is again converted into polyphosphates: water retained in the crystals allows the ends to unwind into long chains with hydroxyl groups at the ends. In the crystallisation of the melt trimetaphosphate is again obtained, with vaporisation of part of the water from the salt mass. On this is based the procedure for the dehydration of melts by alternate crystallisation and fusion.

According to some investigators[40,41] the vapour pressure of water over the melts determines the type of polymers formed and the lengths of the anions present in the melt. Fig. 2 gives the change in the mean chain lengths as a function of the time of holding the melts in air[41]. A melt of dehydrated trimetaphosphate absorbs water from the air and the chains are shortened. The points characterise the change in the melt obtained by dehydration of monosubstituted orthophosphate. The melt loses water in the air and the chains lengthen. After 24 h both melts arrive at the same mean chain length, corresponding to the partial pressure of water in the air. The isotherms shown in Fig. 3 give the decrease in mean length with increase in the partial pressure of water vapour in the atmosphere, At constant pressure a rise in temperature brings about lengthening of the $(NaPO_3)_n.H_2O$ chain, evidently owing to removal of part of the water from the melt.

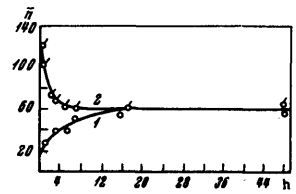

Figure 2. Dependence of the mean chain length ($\bar{n}$) of Graham's salt on the time kept at 650°C at a water vapour pressure of 55.3 torr[4]: *1*) salt obtained from NaH_2PO_4; *2*) salt obtained from anhydrous phosphate.

Prolonged crushing of condensed phosphate crystals or glasses has also been observed[42] to lead to a decrease in chain length. The water from the surrounding atmosphere evidently participates in this process.

The partial pressure of water also affects the relative composition of the dehydration products of crystalline modifications of a single phosphate, as is shown by the example of sodium tripolyphosphate[43]; this is connected with the formation of polyphosphate phases as intermediate compounds; their length is determined by the water vapour pressure. The ability to absorb and liberate water in the formation of different phases is also shown by condensed phosphates of other metals[44–49].

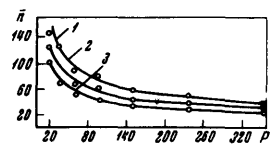

Figure 3. Dependence of the mean chain lengths of sodium polyphosphate melts on temperature and water vapour pressure[41]: Temperatures: *1*) 850°C; *2*) 750°C; *3*) 650°C. $\bar{n}$ = mean chain length; P = water vapour pressure, torr.

The quantitative determination of water present in polyphosphate melts and glasses is difficult and only a few papers‡ give the quantity of water in the melts.

Van Wazer (see Ref. 1, p.593) noted that fusion of NaH_2PO_4 at 700°C gives a preparation of $NaPO_3$ with n = 20–50; on holding the melt at 700–800°C for a month n is increased to 250–500, which corresponds to a water content of 0.07–0.03 wt. %.

‡ For example, according to Owens and Mayer[49] an analysis of a preparation of $NaPO_3$ by the zinc oxide method indicated < 0.2 wt. % H_2O.

The water present in molten metaphosphates is reactive. When molten $NaPO_3$ is held for 2 h at 800°C and then mixed with NaCl, predominantly HCl is liberated. In a melt of KPO_3 + NaCl mixture the liberation of HCl ends after almost 2 h. Judging by the quantity of HCl liberated the formula of the initial preparation was $(KPO_3)_{114}.H_2O$. The preparation of $NaPO_3$ contained more water and the reaction had not ceased after 2 h.[48]

IV. LIQUIDUS DIAGRAMS

1. Metaphosphate–Oxide of the Same Metal Systems

Metaphosphate–oxide systems with a single cation correspond to the sides of the triangle (Fig.1) from the figurative points of the metaphosphates downwards. The diagrams of these systems have been studied mainly by the methods of quenching and thermography; systems with the following oxides have been studied: Li_2O;[50] Na_2O;[51,52] K_2O;[53] MgO;[54] CaO;[55,56] SrO;[57] ZnO;[58] CdO;[59] PbO;[60-62] NiO and CoO;[63] Fe_2O_3.[64] The liquidus curves of all these systems have a chain or ring metaphosphate branch and also diphosphate and orthophosphate branches§.

In systems with Na_2O [51,52] and K_2O,[53] in addition to the diphosphate and orthophosphate branches there is a branch for the tripolyphosphate $M_5P_3O_{10}$; in the system with CaO there is a short branch for a phase of variable composition (tremelite), which was shown to be[65] a hexapolyphosphate with the anion $(P_6O_{19})^{8-}$. In systems with SrO [57] and PbO [66] there are branches for the tetrapolyphosphates $M_3P_4O_{13}$; the analogous Ba compound was obtained from melts and investigated chromatographically[67]. In systems with PbO a compound intermediate between the diphosphate and orthophosphate was also found: $Pb_5P_4O_{15} = 2Pb_2P_2O_7.PbO$.[62] In the systems with CaO, CdO, PbO, Fe_2O_3, and SrO there is yet another compound, different from those mentioned above, and richer in basic oxides than orthophosphates.

In systems with oxides of tervalent elements: B_2O_3,[68] Al_2O_3,[69] and Ga_2O_3 [79] orthophosphates are observed; however, in the diphosphate region only the system with Al_2O_3 has been studied, in which there is a eutectic between $Al(PO_3)_3$ and Al_2O_3. The orthophosphates of Fe^{3+},[71] Al,[72] and B, according to Schulze[73] and to Dachill and Dentglasser[74], are similar in structure to the modifications of SiO_2. According to Van Wazer[1], $AlPO_4$ and BPO_4 are most correctly considered as mixed anhydrides and not orthophosphates. The compound $Bi_3P_4O_{13}$ was isolated and the structure of its anion found chromatographically[68]. In the $Bi_2O_3-P_2O_5$ system, which was investigated by other authors[75] up to 12 mole % P_2O_5, solid solutions based on the high-temperature modification of Bi_2O_3 were found. In the interval between the branches of this phase and of the tetraphosphate there should be a branch of the orthophosphate $BiPO_4$; bismuth diphosphate is stable only in the solid phase.

In systems with the oxides of quadrivalent elements: SiO_2,[76,77] TiO_2,[78] UO_2 [79] there are branches for compounds with the composition of diphosphates: SiP_2O_7, TiP_2O_7, and UP_2O_9. In the first of these compounds various methods have shown the existence of the diphosphate ion[78,80,81,82]. An orthophosphate is not formed in the system with SiO_2; other investigators have not confirmed the report[76] of its formation. The separation of crystalline compounds with composition intermediate between the diphosphate and orthophosphate is characteristic: $Si_2P_2O_9 = SiP_2O_7.SiO_2$; $U_2P_2O_9 = UP_2O_7.UO_2$, close in composition to the $2Pb_2P_2O_7.PbO$ mentioned above[62]. These compounds and others which contain more basic oxide that the orthophosphate do not correspond to the formula of the chain polyphosphates $M_{n+2}P_nO_{3n+1}$.

In the $MoO_3-P_2O_5$ system compounds corresponding to the formulae $MoO_2(PO_3)_2$ (part of the Mo has a lower valency) and $(MoO_2)_2P_2O_7$ have been isolated[83]. As chromatography showed, the first is a polyphosphate with long chains, the second, according to the chemical analysis, is a diphosphate. Compounds of analogous composition but not isomorphous with the Mo compounds are also obtained with WO_3;[83] the composition of their anions could not be found. Schulz's results[83] suggest that the branch of the compounds with the diphosphate formula should extent to the trioxide branch, that is, orthophosphates are not formed in this or in the other system. But since the equilibrium diagrams have not been studied this conclusion needs to be checked.

2. "Metaphosphate–Oxide of Another Metal" Systems

Systems formed from the metaphosphate of one metal and the oxide of another metal constitute the diagonals of the trapezium in the lower part of Fig. 1 and can be represented as sections of the M^I, $M^{II} \parallel O$, PO_3 reciprocal systems. The correctness of this conclusion is confirmed by the experimental results[84-86] on the systems in which M^I = Na or K and M^{II} = Zn: the melts corresponding to the point of intersection of the diagonals appear to be saturated with the same phase (the mixed diphosphate $Na_2ZnP_2O_7$ or $K_2ZnP_2O_7$) irrespective of the initial components: $Zn(PO_3)_2$ and alkali metal oxides, or ZnO and alkali metal metaphosphates. But unlike many well-known salt systems in the present systems both the diagonal sections are stable, that is, they correspond to binary systems having one common branch of mixed diphosphate; its figurative point corresponds to the intersection of the diagonals of the square which represents the reciprocal system. The remaining branches of both sections, apart from the branches of the components, belong to the products of the initial substances—mixed phosphates, which are distinguished in the present systems by the ratio of the cations and even by the anions. In the Na, $Zn \parallel O$, PO_3 system the $NaPO_3-ZnO$ diagonal section[84] has $Na_3ZnP_3O_{10}$ and $NaZnPO_4$ branches (in addition to the branch of the mixed diphosphate); the $Na_2O-Zn(PO_3)_2$ diagonal section[85,86] probably the branches of $Na_2Zn_4P_8O_{25}$ (the structure of the anion was not established) and tentatively, the branch of the mixed orthophosphate. In the K, $Zn \parallel O$, PO_3 system[85,86] on the KPO_3-ZnO and $K_2O-Zn(PO_3)_2$ diagonal sections the compounds $K_3ZnP_3O_{10}$, $KZnPO_4$ and respectively $K_4Zn_3(P_3O_{10})_2$ and (probably) $K_4Zn(PO_4)_2$ are formed.

In the rest of the "$NaPO_3$–basic oxide of another metal" systems studied (M^{II} = Mg;[84] Cd, Pb, Mn;[87] Fe^{3+};[88] Al;[89] Ce, Nd, Sm[90]) mixed salts are also formed: diphosphates (in all the systems with a doubly-charged cation) of the $Na_2M^{2+}P_2O_7$ type; diphosphates with a triply charged cation $Na_6Al_2(P_2O_7)_3$ and $Na_6Ce_2(P_2O_7)_3$; triphosphates $Na_3MgP_3O_{10}$, $Na_3PbP_3O_{10}$, $Na_9Al_2(P_3O_{10})_3$, and $Na_9Fe_2(P_3O_{10})_3$; the orthophosphates of all bivalent metals

§ The system with Fe_2O_3 has not been studied in the range close to $R = 1$. The diagrams of some systems (for example $LiPO_3-Li_2O$) have not been studied in detail: the compounds were obtained by fusing appropriate amounts of the components.

$NaM^{III}PO_4$; the orthophosphates of tervalent metals $Na_3Fe_2(PO_4)_3$ and $Na_3Al_2(PO_4)_3$. It is characteristic that in the Ce and Nd systems mixed orthophosphates are obtained with an excess of the base $(M^{3+}PO_4)_2.Na_2O$. The structure of the compounds with triply-charged cations is probably not reflected in the formula given since tervalent metals can enter into the anion to some extent judging from their role in the Al and B orthophosphates (see above).

In the dissolution of WO_3 and MoO_3 in $NaPO_3$ only one compound (1 : 1) is isolated, as the equilibrium diagram shows [87,91]. A chromatographic investigation of these compounds obtained preparatively somewhat earlier [92] showed them to be mixed orthophosphates of dioxotungsten $(WO_2)^{2+}$ or dioxomolybdenum $(MoO_2)^{2+}$ and sodium.

In the systems mentioned the phases obtained are mixed salts containing both cations. Not one of the diagrams of diagonal sections obtained has branches for compounds formed in the binary systems (that is, represented by points on the sides of the square of the diagram of the reciprocal system). The formation of mixed Na triphosphates by the Mg, Zn, Pb, Al, and Fe^{3+} cations, which do not give triphosphates in the absence of Na, is characteristic. The absence of a mixed diphosphate in the $NaPO_3 - Fe_2O_3$ diagonal section is noteworthy.

The reactions of the compounds which form the equilibrium diagrams of the metaphosphate–oxide systems reflects a characteristic property of the polyphosphate chains to add an oxygen ion. In doing this one initial anion gives two shorter anions and two intermediate groups are converted into two terminal ones. The scanty thermodynamic results suggest that this reaction is exothermic.

However, the formation of a new anion does not always lead to the stabilisation of the diagonal sections. Li and Na [93] and Li and K [94] diphosphates form simple eutectic systems. The diagonal sections of the Li, Na(K) ‖ O, PO_3 reciprocal systems cannot be binary systems, since at oxide concentrations permitting the formation of the P_2O_7 anion instead of the mixed diphosphates characteristic for stable sections the simple ones will be isolated.

As already shown [95] the breakdown of the $P_3O_{10}^{5-}$ anion into $P_2O_7^{4-}$ and PO_4^{3-} leads to the formation of mixed phosphates only when the oxides of doubly-charged cations of small radius—Mg^{2+}, Cd^{2+}, Zn^{2+} (and, according to de Carli [87], also Pb^{2+}) dissolve in sodium triphosphate. When SrO and BaO dissolve, Sr(Ba) diphosphate and sodium diphosphate are obtained separately [95]. Therefore unstable diagonal sections are possible in the Na, Zr(Ba) ‖ O, PO_3 systems. Other phenomena are associated with the instability of the diagonal sections in the K, Na ‖ PO_3, P_2O_7 system [96]; the system passes through the field of the mixed tripolyphosphate $Na_5P_3O_{10}.K_5P_3O_{10}$, the figurative point of which lies off the diagonal sections.

The interaction of $NaPO_3$ with basic oxides does not exhaust the reactions of the compound observed in recording heating curves of annealed melts. When TiO_2, Fe_2O_3, CdO, CuO, PbO, or Sb_2O_3 are held for a long time in $NaPO_3$ melt substances were isolated which could be regarded as products of the replacement of part of the Na in the hypothetical compound $Na_{15}P_7O_{25}$ by another metal; these substances are double decomposition products [97]. During this the melt is enriched in basic oxides, which in one or another form should be separated in further crystallisation of the melt [88].

In the high-temperature treatment of metals by pressure using $NaPO_3$ as lubricant substances were also found [98] which could not be represented as products of the reaction of the metaphosphate with iron(III) oxide but have another polymeric structure.

It has been observed [99,100] that silicon, on being dissolved in $NaPO_3$ melt separates in the form of cristobalite. According to Schwarz [101], notwithstanding earlier statements, silicon does not form a compound with $Na_4P_2O_7$, which separated from the melt as cristobalite. However, $NaPO_3 - SiO_2$ glasses were found by X-ray diffraction [102] to have the P–O–Si bond, that is, are silicophosphates. Thermodynamic calculations also showed experimentally [103] that SiO_2 displaces P_2O_5 from $Ca_3(PO_4)_2$. An even more acid oxide—liquid SO_3—is reported [104,105] to displace P_2O_5 from meta-, tri-, di-, and ortho-phosphates even below 100°C, with the formation of $Na_2S_2O_7$ and $K_2S_3O_{10}$.

3. Systems of Two Polyphosphates with a Common Anion

Systems of two phosphates with a common anion correspond to horizontal sections in the composition triangle (Fig. 1). The common anion in metaphosphates is conventional, therefore at a single figurative point it corresponds to ring phosphates with various n, and chain phosphates. As all the experiments show, these systems are binary. The following metaphosphate systems have now been studied¶: Li–Na, Li–K, Li–Cs, Na–K, [106,107] Na–Ca, [108,109] K–Ca, [110,111] K–Mg, [111] K–Cu, [112] Na–Zn, K–Zn, [113] Mg–Zn, [114] Cd–Zn. [115] In these systems except for the first and the last two, there is a single congruently melting compound $2NaPO_3.KPO_3$, $4NaPO_3.Ca(PO_3)_2$, $2KPO_3.CU(PO_3)_2$ and the 1 : 1 type. In the $LiPO_3 - NaPO_3$, $Mg(PO_3)_2 - Zn(PO_3)_2$, and $Cd(PO_3)_2 - Zn(PO_3)_2$ systems there are extensive ranges of solid solutions up to a continuous series.

These facts show that the formation of mixed polyphosphates is favoured by a difference in the generalised moments of the cations† ($\mu = Z/r$ where Z is the charge, and r the radius of the ion) as in the halide systems in which, during the formation of the compounds, complex anions with covalent bonds are formed to a certain extent. The formation of the compounds $4NaPO_3.Ca(PO_3)_2$, [109,118] $KPO_3.MgPO_3$, and $KPO_3.Ca(PO_3)_2$, [111] which was studied chromatographically, is accompanied by the reorganisation of the anions: all three double salts are trimetaphosphates, whereas $Mg(PO_3)_2$ isolated from melts or glasses is a tetrametaphosphate [19] and $Ca(PO_3)_2$ and KPO_3 have chain anions. Many compounds obtained by fusing oxides with monosubstituted phosphates (for example, by Mehrotra and Gupta [119]) only partly reflected by the equilibrium diagrams in earlier papers, do not contradict the above observations about the connection of the formation of the compounds with the ratios of the crystal-chemical characteristics of the cations.

Polyphosphates do not differ from other salts as regards the conditions of formation of solid solutions. The difference in the anions (chains in $LiPO_3$ and rings in $NaPO_3$), is evidently of no significance, despite the view of Tamman and Ruppelt [120] who associate the absence of solid solutions in the $KPO_3 - NaPO_3$ system with the difference in the anions: $NaPO_3$ is isolated from the melts as trimetaphosphate, that is, with a cyclic anion, KPO_3 as Kurrol's salt, which has a chain anion. The compound which is formed in the $KPO_3 - NaPO_3$ system is similar to that from the system of the sulphates of these metals.

¶ We mention only the most complete investigations.

† Semenchenko [116,117] first showed the value of μ, which characterises the interaction of the species in ionic liquids; we have used this term.

In the Cd, Mg, Zn ‖ PO_3 ternary system, which has been partly investigated[115], solid solutions with $Mg(PO_3)_2$ structure predominate.

In the system of the incongruently melting sodium and potassium tripolyphosphates, which has been studied as a section of the K, Na ‖ PO_3, P_2O_7 reciprocal system[96] the compound $Na_5P_3O_{10}.K_5P_3O_{10}$ is formed it melts incongruently with the formation of solid solutions of diphosphates.

New anions do not arise in the diphosphate systems that have been studied. These systems do not differ from the usual systems with a common anion (see, for example, Refs. 93 and 94).

V. PHYSICAL PROPERTIES OF MOLTEN PHOSPHATES

1. Individual Phosphates

Of the physical properties of molten phosphates, the surface tension σ and the density ρ have been studied most. In 1917 Jaeger[121] first applied a method he had developed for measuring σ and ρ at high temperatures to $NaPO_3$ and KPO_3 melts. Callis and coworkers[122] measured σ and ρ for $NaPO_3$ and calculated the degree of polymerisation by the Eötvös equation in the Foreland form, and using the Sugden parachor, to be 9 and 1 respectively. With allowance for the assumptions made, they considered their results as "weak confirmation of the theory of disordered reorganisation". The values of σ and ρ for $NaPO_3$, KPO_3, and $Ca(PO_3)_2$ explained[123] the decrease in σ along the Ca, Na, K series by the decrease in the "coefficient of extension of the oxygen anion" analogous to that of the generalised moments μ (see p. 866).

Results obtained[124-126] on σ for Li, Na, K, Cs, Ca, Sr, Ba, Zn, and Mg metaphosphates were used for constructing a plot of the surface tension of the metaphosphates against μ for the cations (Fig. 4); the same smooth curve was obtained as for halides, nitrates, etc., but with the difference that unlike these salts there was not a sharp maximum in the region of Sr and Ba. From the curve for the variation of σ for salts with a common cation with the generalised moments of the anions it is found[127] that the value of μ for alkali metal metaphosphates approximately corresponds to the generalised moment of the terminal PO_4^{2-} groups, irrespective of the thermodynamically estimated radius of the orthophosphate ion.

The negative values of the temperature coefficients $d\sigma/dT$ of metaphosphates on an absolute scale are several times less than for other salts. From the values of the temperature coefficients $d\sigma/dT$ the cations of the metaphosphates can be arranged in the following order for the decrease in absolute values of this quantity: K > Na > Ca, and when μ is plotted as a function of the cations a straight line is obtained[123]. This relation was extended[125] to metaphosphates with other cations. $Zn(PO_3)_2$ has[125] a positive $d\sigma/dT$, like B_2O_3 in certain silicates but differing from most of the salts studied. According to Krivovyazov[86] positive values of $d\sigma/dT$ for $Zn(PO_3)_2$ are due to the chains in its melts being mainly connected ("cross-linked") through the Zn atoms, which have fourfold coordinations in this respect.

These ideas follow from the investigations of Zn phosphate glasses[128-130]. With rise in temperature the concentration of the "cross-linked" chains, which are surface active in relation to the other constituents of the melt decreases, which is contrary to the decrease in σ brought about by the decrease in the interparticle interaction as the temperature is raised. The release of Zn from fourfold coordination on heating is also reflected in the volume properties of $Zn(PO_3)_2$. As has been shown[86], the absolute value of $d\rho/dT$ of $Zn(PO_3)_2$ is only a fifth of $d\rho/dT$ of $NaPO_3$ and a tenth the value for the unpolymerised salts. The explanation is that the non-cross-linked chains, the concentration of which increases on heating, permit more compact packing than the "cross-linked" chains, which counteracts the thermal expansion. The more compact packing of the chains is accompanied by greater disorder, which can be explained by a decrease in entropy as the surface increases, which follows from the positive temperature coefficients $d\sigma/dT = -\Delta S$. This explanation is, for $Zn(PO_3)_2$, better founded than the ideas about elongation[131,132], the smoothing out of buckling during the increase of the surface and crumpling of the chains of the surface layer. The formation of the $Zn(PO_3)_2$ surface should take place with liberation of heat, because $\Delta S < 0$. The results[133] on σ and ρ for Li, Na, Ca, and Zn metaphosphates confirms the relation between $d\sigma/dT$ and μ; as Krivovyazov and coworkers[125] found, $d\sigma/dT$ for $Zn(PO_3)_2$ is positive, whereas $Ca(PO_3)_2$ has a small negative temperature coefficient.

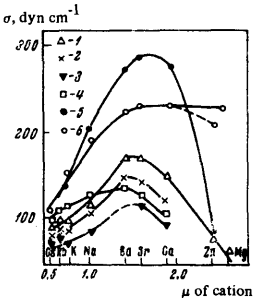

Figure 4. Dependence of the surface tension of metaphosphates on the generalised moments of the cations[122]: *1*) chlorides; *2*) bromides: *3*) iodides; *4*) nitrates; *5*) borates; *6*) metaphosphates.

The internal friction η was studied only for $NaPO_3$; according to Arndt[134] it is 200 times η for NaCl at the same temperature, but only one thirty-fifth that for B_2O_3 heated to 1000°C. The results[135] on η for $NaPO_3$, also calculated by the Bachinskii equation, showed that the viscous flow cell contains not more than eight PO_2 groups—a number close to that found[122] for the degree of polymerisation by the Eötvös equation. Whether the chain segments move separately or the number of PO_4 units in the cell corresponds to a mean length of the reconstructed chains, is thought to be uncertain[122]. On this basis[49,136] it has been found with the aid of the Bachinskii equation that the viscous flow cell contains 30 groups. The values obtained are several orders of magnitude less than found by the investigation of solutions and crystals[137-139].

The vapour pressure of molten phosphates has been studied very little. According to Storonkin and Bobrov's results[140] the vapour pressure of $Al(PO_3)_3$ at 1450°C reaches 115 mmHg. As regards the vapour pressure or dissociation pressure of other metaphosphates there are only notes made in passing that the pressure of some metaphosphate

melts is "insignificant"[49], that dissociation is not noted on heating a melt for 8 h at 1000°C;[141] on the other hand there is a report that above 1000°C "after some time" there is an appreciable loss of P_2O_5;[123] loss of P_2O_5 by calcium metaphosphate has also been noted[55]. Information on the electrical conductivity of molten metaphosphates has been given[142].

2. "Metaphosphate–Oxide" Systems

Of the properties of "metaphosphate–oxide of the same metal" melts the attention of investigators has been mostly directed towards surface and volume properties. The $NaPO_3$–Na_2O system has been studied[122]; the increase in σ and ρ (at constant temperature) with increase in R is explained by the shortening of the chains, this conclusion being drawn from the titration of terminal groups of aqueous solutions of the quenched glasses. Similar conclusions were drawn[123] for the $NaPO_3$–Na_2O, and KPO_3–K_2O systems, studied up to $R = 2$, and the $Ca(PO_3)_2$–CaO system studied up to $R = 1.66$. The slope of the straight lines showing the variation of σ with R increases with increase in μ for the cation. The increase in σ with R is explained by the increase in the "bond density" near the surface. With increase in R there is a decrease in $d\sigma/dT$ for every system‡, that is, the absolute values of $d\sigma/dT$ increase.

A rise in σ with increase in the concentration of the oxide was found in the $Ca(PO_3)_2$–CaO system[143]. An increase in σ with increase in R was also observed for the $Zn(PO_3)_2$–ZnO system[86]; at $R = 2$ a break is found, due[86,143] to the appearance at this concentration of surface inactive PO_3^- anions. The increase in $d\sigma/dT$ on adding ZnO is explained by the favourable action of the oxide on the breaking at elevated temperature of the surface-active "cross-linked" polyphosphate anions. Only on reaching a certain oxide concentration $R = 1.43$, when few "cross-linked" chains are left does $d\sigma/dT$ decrease with increase in R, remaining positive within the range of ZnO concentrations investigated.

σ and the molar volumes v of binary systems of Li, Na, Ca, and Zn metaphosphates and oxides with the same components for compositions with $R = 1$, 1.5, and 1.66 have been studied[133]. The value of σ increases with R for lithium, sodium, and calcium systems; for the zinc system σ was almost independent of R; $d\sigma/dT$, which is negative for the systems with Li and Na and positive for the systems with Ca and Zn, decreases with rise in R. The positive values of $d\sigma/dT$ were thought to be connected with the tendency of Ca and Zn to give covalent bonds with an oxygen atom and also with the fact that at the same values of R in these systems the chain length is greater than in systems which contain Li and Na, as was shown chromatographically[31]. Objections were raised[133] against the application to phosphates of the explanation[144] connecting the $d\sigma/dT$ of silicates with the subdivision of the anions of polymers on heating, since according to the polarographic determination, the anionic composition of polyphosphates varies little with temperature.

In all the studies made the isotherms of the properties investigated do not reflect the formation of alkali metal triphosphates and calcium hexapolyphosphate shown by the equilibrium diagrams. The formation of diphosphates has been noted only in the system with ZnO. The break found[143] in the $Ca(PO_3)_2$–CaO isotherm corresponds to the $(P_4O_{13})^{6-}$ anion.

The shortening of the chains on the introduction into Li, Na, K, and Ca polyphosphates of oxides with a common cation was shown[17] by investigating the infrared spectra of the glasses. The addition of oxides shifts the peak to higher frequencies. These results confirm the above explanation of the dependence of σ on R and μ.

σ and θ of melts of diagonal sections of the Na, Zn ‖ O, PO_3 and K, Zn ‖ O, PO_3 systems have been studied[85,86]. The isotherms of σ for $Zn(PO_3)_2$–K_2O (or Na_2O) sections have minima which differ from the isotherms described above for the binary systems with a single cation. The formation of mixed oligophosphates, shown by the equilibrium diagrams, does, as in the metaphosphate–(oxide of the same metal) systems, not determine the form of the σ isotherm. On adding Na or K oxide to $Zn(PO_3)_2$ σ does not increase—as in the $Zn(PO_2)_2$–ZnO system—but decreases. In the opinion of these investigators[85,86] the decrease is due to the formation of anionic complexes, the nature of which is uncertain, but which are determined by the tendency of Zn to form covalent bonds. In parallel with this there is the shortening of the polymer chains usual on the introduction of an oxide into the melt[144,145]. Starting from a certain concentration the effect of the latter process on σ predominates—σ starts to increase. The course of the temperature coefficients $d\sigma/dT$ can also be explained by its decreasing on adding Na_2O and K_2O but in some concentration ranges it changes very little since as the temperature is raised the surface-active anionic complexes decompose with the formation of inactive ones. The presence of new anionic complexes in the melts is demonstrated by the positive $\Delta\theta$ of mixing, similar to that which is observed in salt systems[146] in which the formation in the melts of anionic complexes with covalent bonds leads to positive values of $\Delta\theta$. The extensive chemical interactions during the dissolution in $NaPO_3$ melt of the oxides of bivalent and tervalent metals also show the excessive changes in free energies noted[147-149] in studying the chemical and concentration cells containing solutions of Pb, Bi, Ni, and Sb oxides in molten $NaPO_3$.

3. Systems with a Common Anion

The Table gives data on the fusion characteristics, the σ isotherm, $d\sigma/dT$, and $\Delta\theta$ for metaphosphate systems. Systems 1, 2, and 3 were classified as ideal by their investigators[152]; the Zhukhovitskii equation[153] in the form given by Guggenheim[154] was taken as a criterion of the ideality for σ; it has shown[141,155] that in most parts of the salt systems with formation of a compound the singular points on the σ isotherms alter. The behaviour (see Table) of system 3 in melts can be placed in accordance with the fact that from the infrared spectra[150] only the components are present in quenched melts, that is, the compounds dissociate during fusion. The same can also be suggested for system 2. Chromatograms of quenched melts of systems 1, 2, and 3 show the additivity of the anionic composition[133]. System 4 represents a change to the systems containing undissociated compounds in the melts; there are no singular points, but there is a negative departure of σ from that calculated by the Guggenheim formula[133,141]. Systems 5 and 7, the diagrams of which show the formation of compounds[86], and also system 6, for which there are grounds for expecting the formation of compounds by analogy with other systems which contain the same cations, have σ isotherms with minima or breaks

‡ Subsequently the increase in the absolute values of negative quantities will also be termed the loss function.

Isotherms of the properties of binary systems of metaphosphates.

No.	System	Type of diagram, compound	σ isotherm	$d\sigma/dT$	θ or $\Delta\theta$ isotherm
1	$LiPO_3$—$NaPO_3$	eutectic [106, 107]	weakly convex to the composition axis	—	straight line [133, 141, 152]
2	$LiPO_3$—KPO_3	$LiPO_3 \cdot KPO_3$ [106, 107]	ditto [152]	—	—
3	$NaPO_3$—KPO_3	$2NaPO_3 \cdot KPO_3$ [106, 107]	ditto [152]	—	convex away from the composition axis [150, 151]
4	$NaPO_3$—$Ca(PO_3)_2$	$4NaPO_3 \cdot Ca(PO_3)_2$ [108, 109]	ditto [133, 141]	—	ditto [133, 141]
5	$NaPO_3$—$Zn(PO_3)_2$	$NaPO_3 \cdot Zn(PO_3)_2$ [86]	minimum at 50 mole % $NaPO_3$	sign change [86]	with inflection [86, 133, 151]
6	KPO_3—$Ba(PO_3)_2$	—	minimum at ~70 mole % KPO_3 [141]	—	—
7	KPO_3—$Zn(PO_3)_2$	$KPO_3 \cdot Zn(PO_3)_2$ [86]	minimum at ~70 mole % KPO_3 [86, 151]	sign change [86]	with inflection [86, 151]
8	$Ca(PO_3)$—$Zn(PO_3)_2$	—	convex away from the composition axis [133]	—	—

(Fig. 5). The chromatograms of systems 4 and 5 show [133] an increase in the chain length on adding the metaphosphate of a bivalent metal to $NaPO_3$ melt. On this basis it is thought [133] that the change in anionic composition during the formation of compounds in polyphosphate melts leads to lengthening of the chain; the constancy of σ in the region of the minima is attributed to constancy of the concentrations of short and long chains.

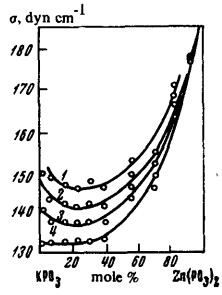

Figure 5. Surface tension of the KPO_3—$Zn(PO_3)_2$ system [86]. Temperature, °C: 1) 800: 2) 900; 3) 1000; 4) 1110.

Melts of systems 4, 5, and 7 are formed from the components with an increase in volume [133]. This is attributed to an increase in the concentration of the long chains under the influence of the doubly-charged cation. According to Krivovyazov [86] the change in $\Delta\theta$ in the last two systems is more complex: at low alkali metal concentrations the $\Delta\theta$ curve is concave ($\Delta\theta < 0$, mixing of the liquid components is accompanied by contraction), at high concentration it is convex away from the abscissa axis ($\Delta\theta > 0$). The shape of the $\Delta\theta$ and $d\Delta\theta/dT$ curves and also the minima on the σ isotherms are explained [86,141,151] by the superposition of effects: the first portions of alkali metal metaphosphate added to $Zn(PO_3)_2$ decrease σ owing to the surface activity of Na (or K) and the formation of surface-active anionic complexes which markedly affect σ. However, during this the volume is not increased§, but reduced, since the destruction of the "cross-linked" $Zn(PO_3)_2$ chains which takes place on the addition of $NaPO_3$ (or KPO_3) has a greater effect than the appearance of a few anionic complexes. Only when there is a high concentration of alkali metal metaphosphates is the concentration of anionic complexes sufficient for the appearance of a $\Delta\theta$ maximum; σ is not sensitive to the appearance of surface-active species, less sensitive to the increase in the concentration of surface-inactive products of the destruction. Only at high alkali metal concentrations does σ increase owing to the accumulation in the melt of surface-inactive cross-linked $Zn(PO_3)_2$ chains and the approach of the composition to pure $NaPO_3$ (or KPO_3).

§ For salts systems in which anionic complexes with predominance of covalent bonds are formed, an increase in volume on mixing is typical [146].

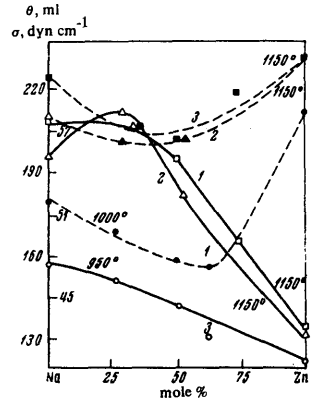

Figure 6. Molar volume (continuous lines) and surface tension (broken lines) of systems of sodium and zinc polyphosphates [133]. R: 1) 1; 2) 1.5; 3) 1.66.

Hence in systems consisting of Zn or Ca metaphosphates and Na or K metaphosphates the change in chain length goes in parallel with complex formation. These connect the phosphate melts with melts of $ZnCl_2$—M^ICl systems [156,157].

σ and θ for binary systems corresponding in composition to the Na and Zn tri- and tetra-polyphosphates have been studied [133]. The nature of the σ isotherms is the same as for systems of the metaphosphates of the same metals (Fig. 6); they have minima. The θ isotherm of the system of tripolyphosphates has a sharply expressed maximum, the system of tetraphosphates a positive departure of θ from a straight line.

The action of Zn and Ca on the change in properties of the alkali metal metaphosphates is thought [133] to be explained solely by the change in the length of the polymeric chains. This point of view is based on chromatographic

results, whereas the conclusion about complex formation[86,151] rests on results of physicochemical analysis. We note that ionic complexes can be decomposed in the dissolution of glasses for the chromatography. Furthermore, the chromatographic behaviour of the polyphosphate ionic complexes is unknown and to deny their existence on the basis of chromatographic results alone is premature.

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Kurnakov Institute of General
and Inorganic Chemistry,
Academy of Sciences of the
USSR, Moscow

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Radiochemical Methods for the Preparation of Organic Derivatives of the Elements

V.D.Nefedov, M.A.Toropova, and E.N.Sinotova

The review deals with the radiochemical procedures for the preparation of organic derivatives of the elements based on the carrier method and also processes occurring in the β-decay of the constituent atoms of the molecular systems.
These methods are particularly important for the synthesis and investigation of the properties of the organic derivatives of elements without stable and long-lived isotopes and also compounds of the inert gases.
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I. INTRODUCTION

The chemistry of organic derivatives of the elements, the "third chemistry"[1], is a branch of science on the borderline between inorganic and organic chemistry. At one time such compounds played an important role in the development of the concept of valence[2] and also in the development of the theory of the structure of organic compounds[3,4]. Nowadays compounds of this class have found wide application in science and engineering and are manufactured on an industrial scale.

The intense development of the chemistry of organic derivatives of various elements began in the USSR at the end of the 1920's. The development of theoretical and practical problems in this field is especially due to Nesmeyanov and his school[5-9]. The establishment of a relation between the ability of elements to form organic compounds and their position in the Periodic System[5,9] led to the discovery of the possible syntheses of organic derivatives of elements which had not been investigated in this respect. These include all the elements with atomic numbers greater than 83 (radioactive elements) and also the inert gases. The relation established by Nesmeyanov can be undoubtedly extended also to radioactive elements such as francium, radium, astatine, and polonium.

II. METHOD OF SPECIFIC CARRIERS

1. Characteristics of the Preparation and Investigation of Compounds of Radioactive Elements

For a long time organic derivatives of the above elements were not prepared because of a number of features encountered in syntheses of radioactive elements[10]. These include, on the one hand, the impossibility of obtaining weighable amounts of individual radioactive elements, even by the most modern methods of nuclear physics, because of their short lifetime (astatine, francium, radon). On the other hand, studies with large amounts of many radioactive elements inevitably involve intense radiation-chemical changes both in the substances themselves and in the surrounding medium. The latter make it impossible to secure

accurate information about the properties and the state of the elements and the nature of the compounds obtained[11,12].

These factors make it necessary to work with extremely small amounts of radioactive elements, which greatly complicates the syntheses in practice and also makes it impossible to establish the composition of the compounds prepared by direct analytical methods. For this reason, the so called method of specific carriers has played a special role in the usual chemical syntheses of compounds of radioactive elements[13-16].

The carrier method is based on the similarity of the properties and behaviour of similar elements and their compounds. Examination of the Periodic Table shows that all the radioactive elements up to element No. 115 inclusive have such close analogues. Therefore the basis of this method is extremely general.

Radiochemical experiments have shown that the data on the behaviour of radioactive elements obtained using submicroscopic amounts and similar elements as carriers adequately reflect the properties of the given radioactive element. Thus the numerous facts established by studies on the chemical behaviour of sometimes even individual atoms of radioactive elements were subsequently confirmed by experiments with macro-amounts of the substance[17,18]. The most striking example in this respect is provided by the design of nuclear manufacturing plant in which the technological isolation of plutonium was developed on the basis of radiochemical investigations of submicroscopic amounts of this element. The scaling-up coefficient on transition to the industrial process was 10^{10}.

The similarity of the properties and behaviour of similar organic derivatives of analogous elements should be even greater. This is because in complex derivatives of this kind the differences between the individual properties of the central atoms are largely obliterated.

Since it is impossible to establish by direct chemical analytical methods the composition of the compounds of the radioactive elements obtained, indirect methods, based on a comparison of the behaviour of the test substances with that of compounds of analogous elements, play a considerable role. In preliminary experiments, the behaviour of compounds of the analogous element is investigated and the data thus obtained constitute the basis for the identification and the determination of the yield of the analogous compound of the radioactive element. Chromatographic methods have proved particularly convenient for this purpose[19-26]. The study of the properties of compounds of radioactive elements based on a comparison with data on the chromatographic behaviour of compounds of analogous elements is widely employed at the present time. In this connection, one can show, for example, that the similar chromatographic behaviour of the trivalent cation of lanthanide and transuranic elements has played a very important role in the identification of americium, californium, and other "far" transuranic elements[27-36].

Numerous compounds of polonium and astatine have been synthesised by the method of carriers[25,37-46].

2. Preparation of Organopolonium Compounds by the Method of Carriers

In view of the position of polonium in the Periodic System and the electronic configuration of its atoms ($6s^26p^4$), it was expected that polonium would form both alkyl and aryl organic derivatives of the following types: R_2Po, R_2PoX_2, R_3PoX, and $RPoX_3$, where R is an organic group and X a halogen atom.

The first studies on the synthesis of organopolonium compounds of the type R_2Po were carried out by Khlopin and coworkers as early as the 1930's for methyl and benzyl derivatives[37-39]. The existence of polonium in the form of an organic compound was proved by the observation that in the recrystallisation of the dibenzyl derivative and in the distillation of dimethyl telluride, polonium behaves analogously to the corresponding tellurium compounds.

Further studies showed that not all the classical methods suitable for organotellurium compounds can be used to prepare organopolonium derivatives[40-42]. The lower thermal stability of fully organic derivatives of divalent polonium of the type R_2Po excluded synthetic methods involving elevated temperatures. For example, the reaction of metallic tellurium with diphenylmercury or the reaction of tellurium chloride with anisole, which give rise to the formation of high yields of tellurium compounds[47,48], gave only 1-5% of the analogous organic derivative in the case of polonium[49]. The tendency towards decreased thermal stability of similar fully organic derivatives with increasing atomic weight of the central atom is well known and has been observed for elements of other Groups[50].

Table 1. Organic compounds of polonium obtained by the carrier method.

R	Type of compound					
	R_2Po		R_2PoX_2		R_2PoX	
C_6H_5	R_2Po	[40]	R_2PoCl_2	[40]	R_2PoCl	[40]
					R_2PoI	[40]
	R_2Po	[41]	R_2PoF_2	[41]		
p-$CH_3C_6H_4$			R_2PoCl_2	[41]	R_2PoCl	[41]
			R_2PoBr_2	[41]		
			R_2PoI_2	[41]	R_2PoI	[41]
p-$CH_3OC_6H_4$	R_2Po	[25]	R_2PoF_2	[41]		
			R_2PoCl_2	[25]	R_2PoCl	[25]
					R_2PoBr	[25]
					R_2PoI	[25]
α-$C_{10}H_7$	R_2Po	[42, 42]	R_2PoF_2	[49]		
			R_2PoCl_2	[49]	R_2PoCl	[49]
			R_2PoBr_2	[49]	R_2PoBr	[49]
			R_2PoI_2	[49]	R_2PoI	[49]

Note. The numerals in the table denote references (Ed. of Translation).

An extremely convenient method for the preparation of aromatic derivatives of divalent polonium consists in the synthesis via a Grignard reagent in the presence of a 2-8-fold excess of the latter. The experiments were performed with amounts of polonium-210 of the order of 10^{-10} g using as carriers tellurium compounds labelled with radioactive tellurium-127.[25,40-42,49]. The use of labelled tellurium compounds as carriers is very convenient, since under these conditions radiometric analysis makes it possible to follow simultaneously the behaviour of both polonium and tellurium compounds. The yields of organic derivatives of divalent polonium were 65-80%. In many cases, by reducing the amount of the Grignard reagent, the relative yield of the organopolonium compounds was increased. Thus the yield of ditolylpolonium in the presence of a 2-3-fold excess of the Grignard reagent exceeded the yield of ditolyltellurium by a factor of 3-5.[41]

Triallylpolonium halides were obtained by the reaction of stoichiometric amounts of tellurium and polonium tetrachlorides with a Grignard reagent. A higher yield of the polonium compound was not observed in this case.

Diarylpolonium dichlorides were synthesised by chlorinating diarylpolonium. Gradual chlorination of a mixture of diarylpolonium and diaryltellurium showed that the latter is chlorinated much more slowly than the analogous polonium compound[49].

Despite the great similarity in the behaviour of the compounds of analogous elements, under certain conditions it is possible to find methods for their separation. In particular, the separation of organic derivatives of polonium and tellurium may be based on the difference between the oxidising properties of the compounds of divalent tellurium and polonium and also on the difference in the chromatographic behaviour of diaryl polonium and diaryltellurium dihalides in certain polar solvents. It has been shown[25,40-42,49] that in general the chromatographic behaviour of tellurium and polonium compounds is almost identical. However, in certain systems (for example, in a 3 : 2 methanol–water mixture) they are completely separated. Organic compounds of polonium obtained by the carrier method are listed in Table 1.

3. Preparation of Organoastatine Compounds

Astatine is immediately adjacent to polonium on the right-hand side in the Periodic System. Since the stability of organic derivatives of polyvalent halogens in Group VII of the Periodic System increases on going from fluorine to iodine, it was reasonable to suppose that astatine, the heaviest halogen, would form organic derivatives in which it would exhibit valence states analogous to those of iodine (III and V).

The most long-lived astatine isotope is astatine-210 with a half-life of 8.3 h. Such a short half-life intensifies the already considerable difficulties of synthesising organic derivatives of this element. The overall duration of synthetic operations must not exceed 3–4 h in this case. Organoastatine compounds were prepared on the basis of the following scheme[44,45,51]:

$$R_2ICl + KI(At) \rightarrow R_2I(At) \xrightarrow{170^\circ} RI(At) \xrightarrow{Cl_2} RI(At)Cl_2 \begin{cases} \xrightarrow{R_2Hg} R_2I(At)Cl \\ \xrightarrow[NaOCl]{} RI(At)O_2 \end{cases}$$

The astatine compounds were separated from the parent substances and analysed by paper and thin-layer chromatography.

III. METHOD OF STABILISATION AND FRAGMENTATION OF PRIMARY MOLECULAR IONS

1. Behaviour of Primary Molecular Species Formed in β^--Decay

A fundamentally new method for the preparation of organic derivatives of radioactive elements is based on the stabilisation and partial fragmentation of the so called primary molecular ions. These ions arise as a result of the β^--decay of the constituent atom in different kinds of molecule.

We shall consider briefly the processes which develop in the β^--conversion of the constituent atoms of molecular systems. The β^--decay of atoms yields isobars of the adjacent elements to the right in the Periodic System according to the following general scheme:

$$^{A}M_z \xrightarrow{\beta^-} {}^{A}N_{z+1} + e^- + \tilde{\nu} \ .$$

If the atom forms part of a neutral molecule or ion, then the initial instantaneous process is the generation of a primary molecular species containing the atom of the new element, for example:

$$C_6H_5{}^{133}I \xrightarrow{\beta^-} [C_6H_5{}^{133m}Xe]^+; \quad {}^{133}IO_3^- \xrightarrow{\beta^-} {}^{133m}XeO_3^* \rightarrow {}^{133m}XeO_3 \ .$$

The new molecular species containing the adjacent element which are produced in this stage have the same structures and electronic configurations as the initial molecule. Subsequent processes undergone by the primary molecular species are associated with the characteristic response of the electron cloud of the initial atom to the sudden change in nuclear charge as a result of the β^--decay (the electron cloud of the parent system is suddenly placed in the field of a nucleus with a new value of z). This inconsistency results in excitation, ionisation, and partial breakdown of some of the primary molecular species[52-66]. The fraction of primary molecular species which break down as a result of excitation and ionisation does not exceed 20%. Investigations have shown that in the case of organic derivatives of the elements this breakdown (fragmentation) involves the splitting off of the organic radical[19,22-24,26,67].

On the basis of a number of characteristic features of the β^--decay process (instantaneous change in nuclear charge and low probability of the interaction of the β^--particle with orbital electrons), an expression was obtained for the probability of the generation of new states of the daughter atom. This expression permits the calculation of the fraction of daughter atoms in excited and ionised states:

$$P_{mn} = \left| \int \psi_m^* \psi_n d\upsilon \right|^2 ,$$

where Ψ_m^* is the wave function of the parent atom in the state m and Ψ_n the wave function of the daughter atom in the state n.

According to the selection rules established by Migdal[53], transitions are possible only between levels differing solely in principal quantum numbers. The formula for the transition probability in the hydrogen-like approximation was obtained by Schwartz[54,63]. Carlson[57-59] and Skorobogatov[68] made the most detailed and thorough calculations of the excitation and ionisation probabilities. The results led to conclusions concerning the relation between the excitation and ionisation probabilities as a function of the valency and the charge state of the atom and also the position of the elements within the limits of the same Group or Period of Mendeleev's System.

According to theoretical considerations and experimental data, the results of calculations for isolated atoms can be extended to processes involving the constituent atoms of molecular systems. Thus, using an expression for the internal wave function of the molecule obtained as a product of the electronic and nuclear functions on the basis of the Born–Oppenheimer approximation (and neglecting, in accordance with the Franck–Condon principle, the dependence of the electronic wave function on the internuclear distance), Wolfsberg[64] obtained an expression for the probability of the transition of the molecular system from one state to another:

$$P_{A \rightarrow B} = P_{a \rightarrow \beta} P_{a \rightarrow b} \ ,$$

where $P_{\alpha \rightarrow \beta}$ is the overlap integral of the electronic wave

function of the initial and final states of the molecular system for the equilibrium internuclear distance in the initial molecule and $P_{a\to b}$ the probability of vibrational and rotational excitations under the action of the momentum of the radioactive recoil in the β-transition. The individual factors in this expression can be calculated independently. The factor $P_{\alpha\to\beta}$ for the molecular system differs little from the analogous factor for the isolated atom [68]. The numerical value of $P_{a\to b}$ can be calculated from the energy spectrum of the recoil atoms, the bond energy, and the rotational-vibrational factor.

If it is assumed that all the electronically excited and multiply ionised states are unstable, the fraction of the residual primary molecular species is determined by the probability of transitions to the ground electronic state and bound rotational-vibrational levels. Since the fraction of the latter corresponds to the transitions in which the recoil energy available for the dissociation of the bond is less than the energy of this bond, the calculations require a knowledge of the energy of the chemical bond involving the daughter atom in the primary molecular species†.

When β-decay leads to isotopes of stable elements, the bond energies can be found experimentally. The estimation of the bond energy in primary molecular species containing atoms of typically radioactive elements or elements of Group 0 may be based on the isoelectronic principle [69,70].

The processes discussed do in fact largely determine the behaviour of the primary molecular species produced in the β-decay of the constituent atoms of isolated molecules‡.

Theoretical and experimental studies on processes in the β-decay of the constituent atoms of molecules in the gas phase do not resolve the question of the fate of the primary molecular species if the molecules of the parent substances are present partly in the condensed phases. Then there is a possibility of a definite change in the electronic states of the parent molecules, of processes involving excitation energy transfer to the surrounding medium, etc., and finally of changes in the nature of the processes in which the primary molecular species take part. At the same time, in condensed phases many changes can be due to processes in which the primary molecular species and their fragments are neutralised by free electrons and the electrons of the surrounding species, by ion–molecule interactions, and by radiation-chemical processes.

It follows from the above that at the present time it is impossible to give a rigorous quantitative explanation of the changes observed in the β-breakdown of the constituent atoms of molecular systems in condensed phases. At the same time the processes occurring in β-conversions of the constituent atoms of molecular systems are of interest for a wide variety of branches of science, including molecular biology, genetics, the science of the origin of pre-biological formations, etc. [71-73] β-Decay processes are particularly important for the development of new research methods and new synthetic pathways.

† In the calculation of the contribution of the transitions leading to bound rotational-vibrational states, it is necessary to consider only breakdown processes of the primary molecular species requiring a minimum expenditure of energy.

‡ Since the lifetimes of the excited states in radiation-induced transitions exceed by 4–5 powers of ten the vibration periods of the atomic bonds, other processes (for example the transfer of excitation energy under conditions excluding intermolecular interaction) cannot play a significant role.

2. The Use of β-Decay Processes for the Development of New Research Techniques

From the standpoint of the development of new research methods, β-decay processes of halogen and tritium atoms, leading to the formation of the inert gas atoms [74-85], are of considerable interest. If these processes occur in molecular systems such as halogen derivatives (except iodine derivatives) and hydrocarbons, then the resulting molecular ions are unstable and their breakdown leads to the formation of free carbonium ions [82-85]. For example:

$$CH_3F \xrightarrow{\beta^-} CH_3Ne^+ \to Ne + CH_3^+ ,$$

$$CT_4 \xrightarrow{\beta^-} CT_3He^+ \to He + CT_3^+ .$$

In principle, these processes make it possible to obtain free carbonium ions of any composition and structure and with any initial localisation of the charge and also to investigate their reactions with substances of different kinds in the gaseous, liquid, and solid phases. The possibility of using β-decay processes to obtain carbonium ions in a free (non-solvated) state has a wide scope for the development of new research methods in organic chemistry. From this point of view, the most interesting is the breakdown of tritium in highly tritiated hydrocarbons, since it is then possible to investigate the reaction of free carbonium ions by radiochemical methods. These studies are at present being vigorously developed in the Department of Radiochemistry of Leningrad University.

3. The Use of β-Decay Processes for the Synthesis of Organic Derivatives of Elements

The β-decay method can be used to obtain and investigate the compounds of any elements the precursors of which are radioactive isotopes undergoing a short chain of β-transformations. For example: $^{125}Sb-{}^{125m}Te$, $^{210}Bi-{}^{210}Po$, $^{133}I-{}^{133m}Xe$, etc. [86-103]

A distinctive feature of the synthetic methods based on the stabilisation and fragmentation of primary molecular ions arising in the β-decay processes of the constituent atoms of molecular systems is the possibility of obtaining neutral and charged molecular species of the daughter element in the matrices of the crystal lattices of the parent substances. This may be of interest from the standpoint of the investigation of the phenomena which occur in molecular systems during β-transformations of atoms, and also from the standpoint of the investigation and preparation of unstable compounds such as di- and tetra-chlorides of zenon and the halides of krypton [104-107], etc. It is also significant that β-decay processes make it possible to obtain radioactive compounds of daughter elements without a carrier, which is important for the investigation of the behaviour of infinitesimal amounts of substances in processes of different kinds, including deep-purification processes.

The study of the processes in the β-transformation of bismuth isotopes in various aryl derivatives resulted in the preparation of all possible types of organic compounds of polonium, containing a wide variety of groups and an essentially new branch of chemistry was created—the chemistry of organic polonium compounds [19,20,22-24,26] (Table 2).

The use of synthetic methods based on β-decay processes is not restricted to typical organic derivatives of the elements. For example, it has been established that, in the β-decay of molybdenum-99 in the hexacarbonyl of this

element, a considerable proportion of the resulting technetium is in the form of a volatile compound. These observations led to the hypothesis that this element forms carbonyls [112,113], which was soon confirmed by direct synthesis of technetium carbonyl [114,115]. The dibenzyltechnetium cation [116] and the pentadienyl derivatives of this element [117] were obtained similarly with the aid of the β-decay process.

Table 2. Organic compounds of polonium obtained by the method of stabilisation and partial fragmentation of molecular ions.

Organic Group	Parent compound	Yield of polonium compounds, %			References
		R_2Po	R_2PoX_2	R_3PoX	
C_6H_5 (phenyl)	R_3Bi	24	15	61	86
	R_5Bi	5	—	95	108
	R_3BiCl_2	—	92	8	86
p-$CH_3C_6H_4$ (p-tolyl)	R_3Bi	32	—	68	19
	R_3BiF_2	—	95	5	109
	R_3BiCl_2	—	69	31	22
	R_3BiBr_2	—	7	93	109
o-$CH_3C_6H_4$ (o-tolyl)	R_3Bi	33	—	67	19
	R_3BiF_2	—	95	5	22
	R_3BiCl_2	—	67	33	22
	R_3BiBr_2	—	27	73	22
m-$CH_3C_6H_4$ (m-tolyl)	R_3Bi	61	—	39	19
	R_3BiF_2	—	94	6	22
	R_3BiCl_2	—	71	29	22
	R_3BiBr_2	—	13	87	22
p-$(CH_3)_2C_6H_3$ (p-xylyl)	R_3Bi	33	—	67	110
	R_3BiF_2	—	95	5	22
	R_3BiCl_2	—	56	44	22, 109
	R_3BiBr_2	—	7	93	22
α-$C_{10}H_7$ (α-naphthyl)	R_3BiCl_2	27	60	7	
		—	93	5	90
p-$CH_3OC_6H_4$ (p-anisyl)	R_3Bi	15	—	75	24
	R_3BiCl_2	—	75	15	24
p-$C_2H_5OC_6H_4$ (p-phenetyl)	R_3Bi	28	—	72	26
$(CH_3)_3C_6H_2$ (mesityl)	R_3Bi	17	33	35	23, 96
	R_3BiCl_2	—	89	11	
p-$NH_2SO_2C_6H_4$ (p-sulphonamidophenyl)	R_3Bi	52	—	48	111

4. The Use of β-Decay Processes for the Preparation of Inorganic and Organic Compounds of the Inert Gases

At the present time the β-decay processes of the constituent atoms in molecular systems attract attention in connection with their possible employment for the investigation of many problems in the chemistry of the inert gases. In particular it was suggested in 1963 that synthetic methods based on β-transformations can be extended to prepare inorganic and organic derivatives of the heavy inert gases [118,119]. The first experimental confirmation of the validity of these ideas came from a study [104] based on the following chain transformation:

$$^{129}I \xrightarrow[1.7\cdot10^7\ \text{years}]{\beta^-} {}^{129m}Xe \xrightarrow[7.15\cdot10^{-9}\ s]{} {}^{129}Xe$$

where iodine-129 was introduced into iodates, periodates, and $KICl_4$ and the Mössbauer emission spectra were investigated. Although the method employed by the authors made it possible to follow chemical changes occurring only in the lifetime of the excited level (about 10^{-9} s), the importance of this investigation is evident.

Several months later a more extensive series of studies on the chemical consequences of the β-decay of the isotopes of iodine in its various compounds was published. The studies were carried out by radioactive methods which permitted not only the identification but also the isolation of the corresponding compounds of radioactive xenon [99-102,119-129].

The use of the β-decay method for the preparation of organic compounds of the inert gases is of special interest [99-102].

Despite the exceptionally rapid progress in the chemistry of the inert gases, the problem of the organic compounds of these elements remained uninvestigated for a long time [130-136]. Nevertheless, long before Bartlett's investigations [137], Nesmeyanov put forward ideas concerning the possible existence of these compounds, their nature, and methods of synthesis [4]. On the basis of the general laws governing the formation of 'onium compounds, Nesmeyanov concluded that organic derivatives of the inert gases should in fact belong to this class of compounds.

Inorganic and organic 'onium derivatives are ionic compounds in which the cations are the molecular groups $H_{9-N}M^+$ and $R_{9-N}M^+$, where R is the organic substituent, N the Group number, and M the atom of a transition element in Groups V–VIII (0). Examples of such molecular groups ('onium cations) for the Second and Fifth Periods are R_4N^+, R_3O^+, R_2F^+, RHe^+, R_4Sb^+, R_3Te^+, R_2I^+, and RXe^+. These groups are isoelectronic analogues of fully hydrogenated and fully organic derivatives of the elements of Groups V–VII and VIII (0).

A fundamentally new method for the preparation of 'onium cations is one based on the β-decay of the central atom in the compound. The formation of 'onium cations in β-decay processes can be represented as follows. If the central atom of an element in Groups IV–VII is present in fully organic derivatives with electronic structures similar to those of the inert gases, the primary molecular ion formed directly in the β-transformation is the 'onium cation of the next element to the right (Table 3).

Table 3. The formation of 'onium cations in the β-decay of fully organic derivatives of elements in Groups IV–VII.

IV	V	VI	VII	VIII
$R_4Pb \rightarrow R_4Bi^+$				
	$R_3Bi \rightarrow R_3Po^+$			
		$R_2Po \rightarrow R_2I^+$		
			$RI \rightarrow RXe^+$	

The subsequent stabilisation by suitable anions of the 'onium cations thus produced leads to the formation of the corresponding 'onium derivatives.

The results of numerous studies have shown that 'onium compounds can form in β-decay processes also by a different pathway. If the central atom forms part of 'onium derivatives of elements in Groups V–VII, then the β-transformation of the central atom, accompanied by partial fragmentation of the primary molecular ion, leads directly to the formation of such derivatives (Table 4).

It follows from the above that 'onium cations of the inert gases can be obtained both from fully organic halogen compounds and their 'onium derivatives containing radioactive halogen atoms.

The first data concerning the existence of 'onium cations in the gas phase were obtained from mass-spectrometric studies on ion–molecule reactions [138-145] and also from studies on the products of the β-decay of iodine and bromine isotopes in certain halogen derivatives [77,80,81,138]. Thus, it has been established that the interaction of the atomic radical-ions of the inert gases and hydrocarbon molecules

results in the formation of molecular ions of the type HE^+ and RE^+ (E = Ne, Ar, Kr, or Xe). Similar ions were detected in the study of processes accompanying the β-decay of radioactive bromine and iodine isotopes in halogen derivatives. These molecular species (HXe^+, HKr^+, RXe^+, etc.) are none other than the 'onium cations of the inert gases and have all the characteristics of this group of molecular ions. These include the donor–acceptor type of bond between the ligand and the central atom, the corresponding inert gas electronic structure of the central atom, the fact that these species are isoelectronic with the fully hydrogenated and organic derivatives of elements located to their left in the Periodic System, and finally the presence of a single positive charge.

Table 4. The formation of 'onium derivatives as a result of the partial fragmentation of primary molecular ions.

V	VI	VII	VIII
$R_4BiX \rightarrow R_4PoX^+ \rightarrow R_3PoX + R^+$			
	$R_3TeX \rightarrow R_2IX \rightarrow RIX + R^+$		
		$R_2IX \rightarrow R_2XeX^+ \rightarrow RXeX + R^+$	

These considerations, which follow from the fact that the ions are isoelectronic with the corresponding neutral species, theoretical calculations, and results of experimental studies, suggest that isolated 'onium cations of the inert gases are quite stable. The bond energy in these ions (we are considering the breakdown of 'onium cations requiring the minimum energy expenditure, in which the charge is localised in the fragment with the smallest ionisation potential) is 2–4 eV according to the data of different workers[139,145]. Similar or even somewhat higher values (due, in particular, to the additional $d_\pi - p_\pi$ bonds in the case of aromatic derivatives) characterise the bond in organic 'onium cations of the inert gases. Thus in those cases where derivatives of the 'onium cations of the inert gases have not been obtained, the reason is other than the instability of the cations themselves.

'Onium cations are a constituent of 'onium derivatives. The other constituent is the anion. In crystals and solutions of these substances the 'onium cations must coexist with the corresponding anions. This implies that in such systems the vacant electronic level of the 'onium cations must lie above the occupied electronic levels in the anions and in the molecules of the medium containing the ions. Therefore, to ensure the stability of the 'onium derivatives, it is necessary to select anions with the lowest possible occupied electronic level (maximum electron affinity) and 'onium cations with the highest vacant level (minimum ionisation potential of the group of atoms comprising the given 'onium cation)[146]. Of the anions satisfying this requirement, one may mention ClO_4^-, BF_4^-, etc. For the 'onium cations, the relation between the position of the vacant electronic level and certain other characteristics is given by

$$J = I + D_0 - D ,$$

where J is the energy of the vacant electronic level of the isolated 'onium cation, determined in this case by the ionisation potentials of the corresponding neutral groups (HXe, RXe, HAr, etc.), I the ionisation potential of the atoms or groups of atoms in which the positive charge is localised during the fragmentation process of the 'onium cation, requiring the minimum energy expenditure, D_0 the bond energy in the neutral species (HXe, RXe, HAr, etc.), and D the bond energy in the 'onium cations HXe^+, etc.

It follows from this relation that, for all these 'onium cations of the inert gases, except HXe^+ and HRn^+, the position of the vacant level is determined by the difference between the ionisation potential of hydrogen and the bond energy D in the corresponding cation, i.e. amounts to 10–11 eV. For the 'onium cations HXe^+ and HRn^+, the position of the vacant level, determined by the difference between the ionisation potentials of xenon and radon atoms and the bond energy, is higher by 1.5–3 eV.[139] These values exceed by a factor of more than two the ionisation potentials of the alkali metal atoms (the radii of whose ions are close to the radii of the corresponding 'onium cations of the inert gases, for example Cs^+ and HXe^+). This in fact probably explains the impossibility of obtaining unsubstituted 'onium derivatives of the inert gases.

The situation is different for certain organic (for example phenyl-substituted) 'onium derivatives of the inert gases such as xenon and radon. For the corresponding 'onium cations, the position of the vacant level is determined by the difference between the ionisation potential of the organic ligand and the bond energy. If one remembers that the ionisation potential of the phenyl group is 9.5 eV and the bond energy of the middle and heavy inert gases in substituted organic 'onium cations of these elements appreciably exceeds the bond energy in the unsubstituted 'onium cations, the position of the vacant electronic level in the substituted cation is found to be 6–7 eV, i.e. approaches the position of the corresponding levels in ammonium and alkali metal ions. Therefore one may hope that ions of the phenyl-xenonium type will coexist with the above anions. These anions (ClO_4^-, BF_4^-, etc.), characterised by high electron affinity, low bonding energy with organic radicals, low polarising capacity, and a large radius, are of interest also from the standpoint of the stability of the 'onium derivatives of the inert gases themselves.

The stability of compounds, including the 'onium derivatives of the inert gases in which we are interested, may be characterised by the difference between the standard free energies of the compounds and their decomposition products. Since in normal reactions the free energy changes due to entropy changes are small, the stability may be characterised by the difference between the enthalpies of formation of the products and the starting materials. Remembering that substituted organic derivatives of the 'onium cations decompose by the general mechanism

$$R_{9-N}MX \rightarrow R_{8-N}M + RX\S$$

and using Hess's law, it is possible to establish a relation between the heats of decomposition and the energetics of individual stages of the thermochemical cycle

$$\Delta H^0 = U + D^+ + E - D - I ,$$

where ΔH^0 is the enthalpy of decomposition of the 'onium derivative, U the breakdown energy of its crystal lattice, D^+ the energy of the dissociation of R^+ from RXe^+ in the substituted 'onium cation, E the affinity of the electron for the atom or group of atoms substituting the anion X^-, D

§ The decomposition of organic 'onium derivatives of xenon should take place by the mechanism $RXeX \rightarrow Xe + RX$.

the energy of the homolytic dissociation of the C–X bond in RX, and I the ionisation potential of the organic group.

Since all the terms on the right-hand side of the above relation are greater than zero, the enthalpy of decomposition of the given substituted organic xenon derivative increases with the electron affinity of X and decreases with the energy for homolytic dissociation of the C–X bond in RX. Since for the above groups of atoms (ClO_4^-, BF_4^-, etc.) the electron affinity is a maximum and the energy of the homolytic dissociation of the C–X bond a minimum, the 'onium derivatives containing the above anions must have an enhanced stability.

On the other hand, the relation makes it possible to estimate the relative stabilities of the 'onium derivatives of particular cations containing different anions. Thus it can be shown that the enthalpies of decomposition of phenylxenonium perchlorate and chloride differ by not less than 100 kcal mole^{-1}. The difference between the heats of decomposition should be even greater for phenylxenonium perchlorate and hydroxide.

Summarising the above findings, one may say that, in choosing a system for stability of the 'onium cation, preference must be given to substituted aromatic 'onium cations of the heaviest inert gases (xenon, radon). For the stability of 'onium derivatives as individual species, it is desirable to choose compounds which contain both stable 'onium cations and anions with a high stabilising capacity.

Since the studies on the synthesis of organic 'onium derivatives of xenon are in the development stage, we shall consider them in greater detail.

From the standpoint of nuclear-physical characteristics, the most suitable isotope for the preparation of organic 'onium derivatives of xenon is iodine-133 obtained by the fission of uranium-235. Iodobenzene and diphenyliodonium salts are promising as the initial molecular systems [147].

Iodobenzene containing the above iodine isotope was obtained according to the following scheme:

$$(C_6H_5)_2ICl + K^{133}I \rightarrow (C_6H_5)_2I^{133}I \xrightarrow{180^\circ} C_6H_5{}^{133}I .$$

Various diphenyl diphenyliodonium derivatives containing iodine-133 were synthesised using the following reactions:

$$C_6H_5{}^{133}I + Cl_2 \rightarrow C_6H_5{}^{133}ICl_2 \xrightarrow{(C_6H_5)_2Hg} (C_6H_5)_2{}^{133}ICl ,$$

$$\xrightarrow{AgOH} (C_6H_5)_2{}^{133}IOH \xrightarrow{HX} (C_6H_5)_2{}^{133}IX ,$$

where X = NO_3^-, HSO_4^-, BF_4^-, or ClO_4^-. The purity of the diphenyliodonium salts was checked by thin-layer chromatography.

The products of the radioactive breakdown of iodine-133 in the test compounds were accumulated in iodobenzene and its solutions, in iodobenze deposited on crystals of potassium perchlorate, potassium tetrafluoroborate, etc., and also in crystals and solutions of various diphenyliodonium salts [99-102,147]. For this purpose, the systems were put in bubblers which were sealed and kept in the dark at 0°C for 2–3 days.

The formation of xenon compounds was demonstrated by comparing the radioactivities of the chemically free xenon formed in the β-decay of iodine-133 in the test systems with the radioactivity of the xenon isolated from solutions of $K^{133}I$¶. A $K^{133}I$ solution is used as a standard because here the entire xenon is present in a free state. In both cases the radioactive xenon was transferred to a radioactivity detector by a carrier gas (argon). The lower activity of the xenon accumulated in iodobenzene and diphenyliodonium salts is evidence that part of the xenon is chemically bound. The fraction of chemically bound xenon was determined by measuring the radioactivity of the free xenon after the decomposition of its compounds by substances containing anions capable of coexisting with the 'onium cations of the heavy inert gases (HCl, HI, KOH).

It has been shown that the breakdown of iodine-133 in iodobenzene leads to the formation of xenon compounds only when the substance is deposited on crystals of the corresponding salts. This is evident from the data in Table 5.

Table 5. The formation of xenon compounds in the β-decay of iodine-133 in iodobenzene*.

System in which products accumulate	Activity ^{133m}Xe			Yield of xenon compound
	free	bound	overall activity	
$C_6H_5{}^{133}I$	11500±300	not detected	11020±300	0
0.1% soln. of $C_6H_5{}^{133}I$ in benzene	10830±300	ditto	11020±300	0
0.1% soln. of $C_6H_5{}^{133}I$ in chloroform	9420±200	»	9600±200	0
$C_6H_5{}^{133}I$ — $KClO_4$	2820±50	580±10	1670±30	30±3
$C_6H_5{}^{133}I$ — KB $(C_6H_5)_4$	3360±50	740±10	4250±100	18±1
$C_6H_5{}^{133}I$ — KBF_4	1645±30	145±10	1670±30	8±1
$C_6H_5{}^{133}I$ — K_2SO_4	26910±300	1420±30	27100±300	5±1
$C_6H_5{}^{133}I$ — KNO_3	4310±60	180±15	4250±100	4±1
$C_6H_5I^{133}$ — KCl	26310±300	not detected	27100±300	0

*The figures in the second, third, and fourth columns are average values from 5–7 determinations of the yields of the xenon compounds.

The results of experiments on the accumulation of xenon in crystals and solutions of various diphenyliodonium salts are presented in Table 6, which shows that the xenon compounds are not observed when the products are accumulated in crystals and aqueous and hydrochloric acid solutions of diphenyliodonium chloride. In all other cases a considerable proportion of the xenon was present in a chemically bound state.

Further studies were undertaken to elucidate the nature of the xenon compounds (the identity of the chemical state of the xenon formed in the β-decay of iodine isotopes in iodobenzene and in diphenyliodonium salts, proof that xenon forms part of the cation, demonstration of the similarity between the behaviour of the xenon compound obtained and that of the 'onium derivatives of other elements).

To demonstrate that the xenon compounds investigated are of the 'onium type, i.e. that they contain a cationic group incorporating xenon, ion-exchange chromatography and ionophoresis were employed. The chromatographic behaviour of the xenon compounds was investigated in a 2 × 105 mm column filled with Dowex-50X-12 resin (in the H^+-form, 200–400 mesh). The eluent consisted of perchloric acid solutions of different concentrations (Table 7). The elution curves for the xenon compounds formed in the β-decay of iodine isotopes in iodobenzene and diphenyliodonium perchlorate are presented in Figs. 1 and 2.

The ionophoretic behaviour of the xenon compounds was studied in a multicell apparatus of type OE-100, the electrophoretic chamber of which consisted of five cells separated by semipermeable "kutizin" membranes. The outer pairs of cells were filled with 0.001 N perchloric acid and

¶ If the products were accumulated in crystals of the parent substances or in liquid substances deposited on salt crystals, the solid phase was dissolved immediately before the measurement of the radioactivity of free xenon.

the central cells with the solution of the test compound in perchloric acid of the same concentration. The phenylxenonium cations decompose at the cathode with liberation of free xenon. The carrier gas flowing through the cathodic cell passes through a collector and then to a counting chamber. The electrophoretic behaviour of diphenyliodonium cations was investigated at the same time. The results of these experiments are presented in Fig. 3.

Table 6. The formation of xenon compounds in the β-decay of iodine-133 in diphenyliodonium salts.

Accumulation conditions	Yield of Xe compound, %
0.05% soln. of $(C_6H_5)_2ICIO_4$ in 0.1 *N* $HClO_4$	35 ± 3
0.05% soln. of $(C_6H_5)_2IBF_4$ in 0.1 *N* HBF_4	22 ± 2
0.05% soln. of $(C_6H_5)_2IHSO_4$ in 0.1 *N* H_2SO_4	10 ± 2
0.5% soln. of $(C_6H_5)_2INO_3$ in 0.1 *N* HNO_3	6 ± 1
0.05% soln. of $(C_6H_5)_2ICl$ in 0.1 *N* HCl	0
Crystals of $(C_6H_5)_2ICIO_4$	22 ± 2
Crystals of $(C_6H_5)_2ICl$	0

The sum total of the data obtained in the study of the chromatographic and ionophoretic behaviour of the test xenon compounds permits the following conclusions:

(1) The sorption of the test xenon compounds on a cation exchanger and its migration towards the cathode are evidence that xenon forms part of a cationic group;

Table 7. Chromatographic behaviour of organic 'onium cations of xenon and iodine (percentage elution of the cations).

Eluent	Onium cation	Volume of eluent (in free volumes), %																	
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
H_2O	$C_6H_5Xe^+$					is not desorbed														
	$(C_6H_5)_2I^+$					ditto														
0.1*N* $HClO_4$	$C_6H_5Xe^+$					»														
	$(C_6H_5)_2I^+$					»														
1*N* $HClO_4$	$C_6H_5Xe^+$	0	39	48	9	3	1	0												
	$(C_6H_5)_2I^+$					is not desorbed														
3*N* $HClO_4$	$C_6H_5Xe^+$	0	41	44	12	2	2	0												
	$(C_6H_5)_2I^+$															5	12	11	11	
5*N* $HClO_4$	$C_6H_5Xe^+$	0	40	43	11	4	2	0												
	$(C_6H_5)_2I^+$										7	14	14	11	11	11	8	7	7	
7*N* $HClO_4$	$C_6H_5Xe^+$	0	45	48	6	1	0													
	$(C_6H_5)_2I^+$	0	0	8	10	15	14	14	12	9	7	5	4	2	0					

(2) the identity of the chromatographic behaviour of the xenon compounds produced in the β-decay of iodine in iodobenzene and diphenyliodonium salts indicates that in both cases the same xenon compound is formed.

On the basis of the general relations governing the chemical changes following β-transformations of atoms in fully organic and 'onium organic derivatives and also mass-spectrometric data, one may conclude that in this case the cation is $(C_6H_5Xe)^+$.

The possibility of the formation of a xenon cation as such is excluded by the position of its vacant electronic levels. This is consistent with the failure of experiments designed to obtain the corresponding xenon compounds by the radioactive breakdown of iodine in the compound $C_6H_5^{133}I(ClO_4)_2$.

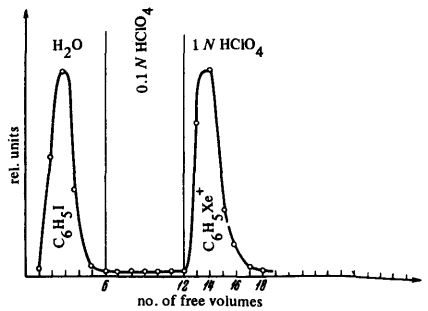

Figure 1. Elution curves of the xenon compound formed in the β-decay of iodine-133 in iodobenzene.

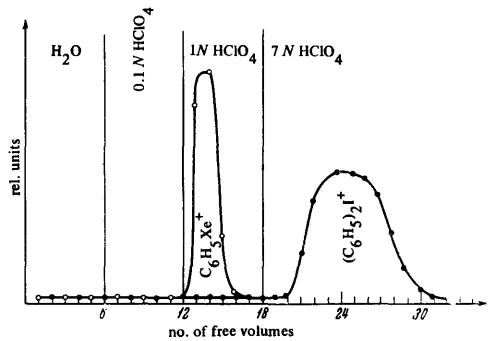

Figure 2. Elution curve of the xenon compound formed in the β-decay of iodine-133 in diphenyliodonium perchlorate.

It is important to note that the processes involving molecular ions formed in β-decay in molecular systems may be determined to a large extent. Thus, by selecting the isotopes of the parent elements with a definite mode of radioactive decay, the type of the initial compounds, and the nature of the substituents, and also by varying the conditions in which the breakdown takes place, it is possible to obtain definite compounds of the daughter elements. In particular mention should be made of the possibility of influencing the processes involving primary molecular ions by introducing substituents of various types into aromatic groups[23,24,26]. This is because electron-donor substituents increase the stability of the primary molecular ions (the yield of the stabilisation product increases at the same

time), while electron-acceptor substituents decrease the stability (the yield of the stabilisation products falls). Since the Hammett equation is applicable to processes involving primary molecular ions formed in the β-decay, it is possible to predict, without resorting to experiments, the fraction of the primary molecular ions which persist and hence also the yield of the products of their stabilisation and partial fragmentation.

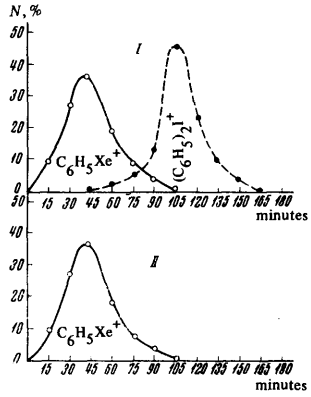

Figure 3. Electrophoretic curves for the xenon compounds formed in the β-decay of iodine-133 in diphenyliodonium perchlorate (I) and iodobenzene (II); N – the fraction of ions which have migrated to the cathodic compartment.

In conclusion we may note that further studies on organic compounds of the inert gases should be designed both to extend the range of investigations in the field of the chemical changes occurring in β-decay processes of halogen isotopes and also to obtain organic derivatives of the inert gases by the usual methods of chemical synthesis.

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Department of Radiochemistry,
Leningrad State University

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Nucleophilic Addition of Amino-groups to an Activated Carbon-Carbon Double Bond

S.I.Suminov and A.N.Kost

The review presents data on the effect of structural and steric factors, catalysts, and solvents on the mode and rate of condensation of activated olefins with amines, which indicate that the mechanisms of such condensations are to some extent general. The considerable importance of the steric inhibition of the reactions is evidence in favour of the hypothesis of a polar transition state characterised by a rigid structure. Proton transfer involving a proton donor and (or) acceptor or, more rarely, the ejection of a negative ion (see the reactions of β-halogeno-olefins) plays a significant role in the stabilisation of the transition state. The sequence of relative activities of the olefins $CH_2 = CHX$ is affected both by the polarising effect of the group X and the possibility of the delocalisation of the charges in the activated complex. Nevertheless the problems of the catalytic effect of proton-donating, alkaline, and particularly peroxidic additives are still not completely clear and require further study.
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1. INTRODUCTION

Reactions involving the addition of amines to an activated carbon–carbon double bond are widely known and are used in numerous syntheses (amino-nitriles, amino-acids, are various heterocyclic structures). The available reviews (the addition reactions of acrylic acid and its esters [1,2], acrylamide [3], vinylpyridines [4], and nitro-olefins [5]) are confined largely to the statement of the facts and the noting of a typical reaction conditions.

Usually the Michael reaction takes place in the presence of alkaline agents, i.e. via the formation of carbanions from the CH component with subsequent nucleophilic attack on the olefin [6]; on the other hand, for the condensation of compounds containing an amino- or imino-group, examples of non-catalytic reactions and of processes catalysed by both acids and bases or accelerated by the addition of proton-donor solvents have been described. Recently studies of the kinetics of these reactions have begun to be published. So far they have dealt with a narrow range of objects (particularly solvents) and the results cannot be correlated. Nevertheless the accumulation of experimental data, both preparative and kinetic, permits certain generalisations.

In this review attention is drawn to the effect of the medium, the catalytic additive, and steric factors in the structure of the amine (or imine). Heterocyclic imines such as pyrrole, indole, and phenothiazine and also acid amides are not considered as the amino-components since their alkylation by olefins usually takes place in the presence of alkaline additives (i.e. under typical conditions for the Michael reaction) via the formation of an anion at a nitrogen atom.

The capacity of unsaturated compounds of the type $CH_2=CHX$ for electrophilic addition is determined by the polarisation of the double bond under the influence of the electron-acceptor substituent X. Furthermore the reactivity is influenced by the type of the nucleophilic component and the polar and steric interactions in the transition stage. Thus, judging from the values of L_β (the localisation energy of the nucleophilic group), calculated for the anionic polymerisation of a number of monomers [7], we have the following sequence: nitroethylene > 2-nitropropene > acrylonitrile > methacrylonitrile > methyl vinyl ketone > methyl acrylate. However, a different sequence is usually found in the Michael condensation [6]: acrolein > vinyl ketones > αβ-unsaturated ethers ≥ acrylonitrile > > vinyl sulphones. A recent study of the kinetics of the reaction of alcohols with vinyl compounds [8] established that acrylonitrile is much more reactive than acrylates. Therefore, wherever this is allowed by the available data, we attempted to compare the nucleophilic properties of amines of different classes in relation to a given olefin †.

† See, for example, Ibne-Rasa [9], concerning the differences between the terms "nucleophilicity" and "basicity" (as applied to amines and imines) and also the conditions under which they have the same significance.

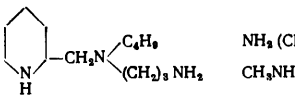
2. ACRYLONITRILE

Lower primary and secondary amines and also diamines are cyanoethylated with formation of mono-derivatives without catalyst at room temperature. With increasing length of the aliphatic group, the rate of reaction of the amines with acrylonitrile falls somewhat (probably due to a decrease in nucleophilic character) and brief heating is required to accelerate the process [10,11]. This method can be used to cyanoethylate a wide variety of amines containing up to 10–18 carbon atoms, benzylamines with ring substituents [12], arylalkylaminomethanes [13-15], etc. No difficulties are encountered in the reaction involving the simplest cyclic (polymethylene) imines: ethyleneimine, pyrrolidine, piperidine, morpholine, and their derivatives in which the NH group is sterically accessible [16,17].

Branching of the aliphatic chain of the amine hinders its cyanoethylation and to a greater extent when the branching point is closer to the amino-group [18-21]. This is shown most clearly for 2,2-disubstituted compounds of the type of t-octylamine [22,23]. Nevertheless the same amines behave normally in alkylation by alkyl halides. Another typical example is provided by 2,6-dimethylpiperidine with two substituents in the α-position relative to the imino-group [24]. In order to cyanoethylate amines with a sterically hindered amino-group, it has been suggested that water, lower alcohols, organic acids [21-26] and catalytic amounts of hydrochloric acid [22] be added to the reaction mixture or that the syntheses be simply carried out in a homogeneous aqueous solution. To increase the solubility of the amine in water, a second solvent may be added (dialkylamides, t-alkylaminopropionitriles, etc.), which in many cases increases significantly the yield [21,26]. It has been stated [27,28] that the cyanoethylation of various higher polymethyleneimines (starting with hexamethyleneimine) is also accelerated by Triton B (40% solution of trimethylbenzylammonium hydroxide). However, so far it is not clear whether the true catalyst is not in fact water, the mole fraction of which in the whole solution is 14/15.

Further studies elucidated the active role of the solvent also in the cyanoethylation of sterically unhindered amines [29-35]. It was established that the addition of the amino-group to the double bond of acrylonitrile is greatly accelerated by proton-donor substances of various classes (water, alcohol, glycols, formamide, organic acids, ammonium salts, ion-exchange resins). The most powerful promoting agent is water, which remains active also in mixtures with inert additives or in mixed solvents. Alcohols catalyse the reaction somewhat less, the promoting effect decreasing on going from methanol to higher members of the series. Branched-chain alcohols (isopropyl and s- and t-butyl alcohols) activate these reaction to only a slight extent [21,31]. Regardless of their polarity and chemical nature, all aprotic solvents (benzene, toluene, cyclohexane, ethyl methyl ketone, dioxan, tetrahydrofuran, ethyl and butyl acetates, acetonitrile, triethylamine, pyridine, etc.) under comparable conditions inhibit the addition of amines and hydrazines to an activated carbon–carbon double bond [29,31]. These findings are confirmed by data on the preparative cyanoethylation of methyl-, hexyl-, nonyl-, and decyl-amines in various media [33-35].

Comparison of the temperature conditions or yields for amines of different classes (primary and secondary aliphatic amines and cyclic imines) (for example, on the basis of the tables in the review of Terent'ev and Kost [10]) leads to the conclusion that a primary amino-group is the most active in the cyanoethylation reaction although the difference is usually small. This is consistent with the lower basicity of primary amines compared with secondary amines (see, for example, Girault-Vexlearchi [36] and Albert and Serjent [37]). When the molecule of the substance cyanoethylated contains various amino-groups, this difference may become distinct. Thus in the cyanoethylation of the triamine (I) [15] the product of addition to the cyclic amino-group was obtained almost quantitatively:



(I)

$NH_2(CH_2)_2N(CH_3)CH_2CH_2CN$ (II)

$CH_3NH(CH_2)_2NHCH_2CH_2CN$ (III)

The cyanoethylation of *N*-methylethylenediamine [38] leads to a mixture of nitriles (II) and (III) in proportions of 73 : 27.

In many cases steric factors can cause a sharp "reversal" of the relative reactivity. On being refluxed with acrylonitrile, 2-amino-1-isopropyl-amino-2-methylpropane forms a 2-cyanoethyl derivative (IV), with the cyanoethyl substituent attached to the NH_2 group and not the imino-group, the steric accessibility of which is much lower [39]:

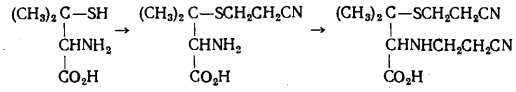
$(CH_3)_2CHNHCH_2C(CH_3)_2NHCH_2CH_2CN$ (IV)

The introduction into the structure of an aliphatic amine of a substituent with a terminal nitrile or ester group lowers appreciably its basicity [40-42]. This effect is particularly marked for CH_2CN and $(CH_2)_2CN$ groups. Thus while the esters of α- and β-amino-acids are cyanoethylated, albeit with difficulty, on being refluxed without catalyst in an inert solvent [43], there is virtually no cyanoethylation in the case of $RNH(CH_2)_2CN$, when R is an alkyl group with more than four carbon atoms [44]. However, the addition to the reaction mixture of methanol or ethanol (or their mixtures with water) greatly facilitates the dicyanoethylation of higher amines [33-35]. Acetic, propionic, and other organic acids have been recommended for the same purpose [45,46]. It is reasonable to suppose that the type of catalysis in these cases is similar to that obtaining for aliphatic amines [30,31].

Successful cyanoethylation of amino-acids requires the formation of an uncharged amino-group from the dipolar ion by the addition of, for example, at least an equivalent of an alkaline agent or a tertiary amine. When the content of alkali is low, the rate of reaction is proportional to its concentration. When an alkali metal salt of the amino-acid in aqueous solution is employed, the corresponding *N*-cyanoethyl derivatives are formed in almost quantitative yields even at room temperature. When the amount of acrylonitrile is raised to 2–3 moles, dicyanoethylation products can also be obtained after refluxing for a short time [43,47].

The study of the cyanoethylation of mercapto-acids and amino-acids of similar basicities showed [48] that in general mercaptide ions are much more nucleophilic than the amino-group. However, the relative rates of reaction involving mercapto- or amino-groups depend on the structure of the compound and may vary from 1300 to 6–8. Thus in the case of dimethylcysteine (penicillamine) the mercapto-group reacts first, but, when the amine : acrylonitrile ratio is 1 : 1, the NH_2 group is also involved to some extent [48,49]; in the presence of acrylonitrile (at a slightly

elevated temperature) satisfactory yields of *NS*-dicyanoethyldimethylcysteine were obtained[50]:



Similar relations involving the ease of cyanoethylation of mercapto- and amino-groups are typical also for other classes of organic compounds‡. For example, the cyanoethylation of 2-aminoethanethiol in an alkaline solution yields a mixture of *NS*-dicyanoethyl and *NNS*-tricyanoethyl derivatives; in a strongly acid medium the reaction does not take place. On the other hand, in the pH range 3.6–6.8 there is a possibility of the selective formation of 3-(2-aminoethylthio)propionitrile[51].

The cyanoethylation of aromatic amines with acrylonitrile encounters considerable difficulties owing to the low basicity of the amino-group (pK_b = 8.5–11.5). However, it is stated in patents that acrylonitrile can add non-catalytically to the most basic representatives of the series, namely to *p*-phenylenediamine[52] and *N*-hydroxyethyl-*m*-toluidine[53], but these findings have not been checked. Aniline is recovered unchanged after prolonged refluxing with acrylonitrile at 180°C[54,55].

The available methods for the cyanoethylation of aniline, its *N*-substituted derivatives, and homologues can be divided into three groups: (a) reactions in the presence of acid reagents; (b) reactions catalysed by copper salts; (c) reactions in proton-donor solvents§. Organic acids and their anhydrides, dialkylammonium and aluminium salts, and, with poorer results, inorganic acids, have been used as the acid catalyst[44,58–61].

The reaction can be conveniently carried out in the presence of added acetic acid and an excess of acrylonitrile with refluxing for 6–24 h, the product being the monocyanoethyl derivative and in rare cases also an admixture of the bisadduct. The yields increase if a large amount of acetic acid is added, since the latter can be used also as a high-boiling solvent[61]. It is possible to establish (albeit only approximately, since the basicity does not always correspond to nucleophilicity) a relation between the basicity of the aromatic amine and the ease of its cyanoethylation[59,61]. For compounds with very low basicity (for example diphenylamine and α- and β-aminoanthraquinones), the yields of the corresponding *N*-cyanoethyl derivatives do not exceed 10–15%; nitroanilines do not combine with acrylonitrile in acetic acid at all[61]. As a rule, for the same basicity, amines containing substituents at the nitrogen atom or in the *ortho*-position relative to the amino-group are cyanoethylated much less satisfactorily (because the reaction centre is sterically hindered).

Contradictory views have been expressed in the literature concerning the catalytic effects of the salts of copper, zinc, cobalt, nickel, iron, and chromium in different valence states and even of metallic mercury on the addition of acrylonitrile to aniline and its substituted derivatives[61–63]. The main practical use has been of copper acetate (or its hydrate), which can catalyse vigorously the monocyanoethylation of various anilines without acid additives[61].

‡ On the other hand, ethanolamine, its *N*-substituted derivatives, and other amino-alcohols are cyanoethylated exclusively at the amino-group without alkaline additives[10].

§ We exclude from consideration the rare examples of the cyanoethylation or aromatic amines in the presence of alkaline reagents (choline hydrate, Triton B, carbazolylpotassium)[44,56,57] for reasons stated above.

The reaction takes place when a mixture of the reagents is refluxed (2–12 h), but sometimes, after a thermal initiation stage, the temperature of the reaction mixture rises spontaneously by 10–15 deg¶.

A characteristic feature of the method is its low sensitivity to the position of the substituent in the ring and to the size of the *N*-alkyl substituent. Even *m*-nitroaniline is readily cyanoethylated in the presence of copper acetate but the *para*-isomer, the basicity of which is low, reacts much less well[61].

Specific co-catalysts of the dicyanoethylation of aromatic amines in acetic acid are copper(I) cyanide and chloride and cobalt (II) chloride[44,62]. The use of the most active of these (Cu_2Cl_2) permits the synthesis, in the presence of only a small excess of acrylonitrile, of dicyanoethyl derivatives of various anilines (including anilines containing electron-acceptor substituents). However, the limitations associated with the steric screening of the reaction centre remain effective. Thus, among *ortho*-substituted amines, only *o*-toluidine gives a dicyanoethyl derivative in a yield up to 35%, while α-naphthylamine and *o*-aminobiphenyl form only monoadducts.

During the last ten years a preparative method has been developed for the cyanoethylation of aniline and its *para*-substituted derivatives in the presence of water as the catalyst[55,65–67]. The yields and the rates of the reaction are determined both by the basicity of the amine and its solubility in water. An almost quantitative yield of 3-phenylaminopropionitriles can be achieved by carrying out the reaction in an aqueous solution, provided that the aniline and the acrylonitrile are fully soluble[66]. The yield of adducts is in most cases unaffected by the variation of the pH of the medium in the range 6.8–10.8.[67,68] Refluxing for 1–5 h with a slight excess of acrylonitrile in aqueous solution also results in the formation of the *NN'*-dicyanoethyl derivative of *p*-phenylenediamine and the monoadducts of *NN*-dimethylphenylenediamine and *o*-toluidine, although in the latter case the yield does not exceed 30%. However, the attempts to cyanoethylate nitroanilines even under more severe conditions (heating in a sealed tube at 150°C) were unsuccessful[69]. On the other hand, heterocyclic imines (pyrazolines, tetrahydroquinolines, aminopiperidines, etc.), whose basicity approaches that of aromatic amines, can be successfully cyanoethylated in the presence of water[30,70–72].

Butskus[73] showed that aliphatic diols and many phenols can be used as solvents for the cyanoethylation of aromatic amines. Thus phenols, hydroquinone, and naphthols (8–9 g per 0.1 mole of aniline) give rise to 98–100% yields after refluxing for 20 h with an excess of acrylonitrile, while ethylene glycol may be recommended as a solvent in preparative syntheses. However, the catalytic activity of lower aliphatic alcohols proved to be slight.

3. MECHANISM OF THE CYANOETHYLATION OF THE AMINO-GROUP

Numerous examples of appreciable steric control of the reaction, of the role of the polarity and the proton-donor

¶ There exists no definitely formulated view concerning the mechanism of the catalysis by metal salts of reactions involving the addition of an amine to the double bond of acrylonitrile and acrylic esters. The hypothesis that a Π-complex of the unsaturated compound with the metal cation takes part in the reaction appears to be the most likely[64].

properties of the solvent, and the possible acid catalysis can all be interpreted only on the assumption that the cyanoethylation of the amino-group (and related reactions) takes place with intermediate participation of ionic species. Earlier it was assumed that these are 1, 4-addition reactions[74,75]. Terent'ev and Kost[10] believed that the cyanoethylation involves the formation of an amine—acrylonitrile complex which rearranges to the corresponding adduct by intramolecular migration of a proton. Later Heininger[61], Luskin et al.[22], and also Bekhli[55,56] explained the sharp acceleration of the cyanoethylation of aromatic amines and t-alkylamines in the presence of various catalysts and water by postulating the protonation of the nitrile group of acrylonitrile by proton-donor elements of the medium:

$$\overset{+\delta}{CH_2}{=}CH{-}\overset{+}{C}{\equiv}N + H^+ \longrightarrow \overset{+\delta_1}{CH_2}{=}CH{-}\overset{+}{C}{\equiv}\overset{+}{N}H \qquad +\delta_1 > +\delta$$

The additional shift of electron density then occurring increases the electron deficiency at the terminal carbon atom in the double bond and consequently the alkylating activity of acrylonitrile. Similar views were put forward by workers who investigated the addition of acrylic acid esters to amines (see, for example, Baltrusis and Macinlis[76]).

Nevertheless, analysis of the experimental data currently available shows that these hypotheses are inadequate[29]. The point is that the cyanoethylation of aniline in the aqueous phase takes place most satisfactorily[67,68] at pH 6.8–8.8 and therefore does not require either alkaline or acid catalysis. Furthermore, an increase or decrease of the pH from the optimum value results in a decrease of the yield. In a study of the kinetics of the addition of acrylic acid esters to cyclic imines in protic solvents the catalytic effect of acid additives was also not observed[68,77,78]. The addition of acids in the cyanoethylation of sterically unhindered aliphatic amines usually does not facilitate but actually hinders the reaction. In reactions with aromatic amines the replacement of acetic acid by phosphoric or hydrochloric acid somewhat inhibits the process[59,65]. Furthermore, it is known that the catalytic effect of water and alcohols in cyanoethylation reactions is not fully correlated with their acidity. Thus methanol is a stronger acid than water (by a factor of 1.5–3 according to different estimates[79]) but it promotes the addition of amines to an activated double bond to a lesser extent[31]. The sharp fall of the yield of cyanoethylation products in alcoholic media on going from methanol to higher homologues and in particular to branched-chain alcohols shows the considerable role which steric factors play, together with acidity, in the catalytic capacity of alcohols[21,29,31].

In addition, nitriles, esters, ketones, and even amides are weak bases which are hardly protonated by weak acids[80]. On the other hand, when the molecule contains a conjugated carbon–carbon double bond, the basicity of a functional group of this type is even lower, and, for example, acrylonitrile in 85% sulphuric acid is only 50% protonated[81].

Thus, under cyanoethylation conditions, acid additives should affect primarily the amino-group of the amines alkylated (which is present in a considerable excess relative to the acid). On the other hand, in the presence of water or alcohol the reversible protonation of the nitrile group when an amine is also present becomes altogether unlikely. One is virtually driven to the conclusion that only hydrogen bonds with participation of ammonium or oxonium salts are formed[82].

Finally, there is no unambiguous proof whether the activity of the carbon–carbon double bond is at all significantly increased (the electrophilic properties are increased) when the functional group of acrylic monomers is protonated[83,84]. Furthermore, hydrogen bonds formed between the solvent and the amine reduce the nucleophilicity of the amino-component and therefore must compensate the effect of monomer activation[85].

Without disproving completely the role of the protonation of the functional group in the activation of $\alpha\beta$-unsaturated compounds, the above findings show that this phenomenon cannot be responsible for the exceptionally high catalytic effect of the solvent.

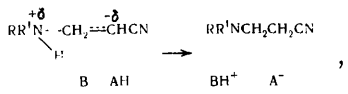
The available data are best explained on the assumption that the process takes place via an activated complex characterised by an appreciable or complete charge separation[21,29-31,50]. The probability of the formation of such an activated complex depends on the polarity of the medium. If the intermediate state is more polar than the initial components, then the reaction does not occur (or occurs with difficulty) in polar solvents[85]. This is probably so in our case. The polarity of amines is relatively low ($\epsilon = 3-7$) and, as their concentration in the mixture increases, the polarity of the medium falls[86,87]. The introduction of a protic solvent (water, alcohols) maintains the dielectric constant of the solution in the range 20–60 D. On formation of the transition state and its further stabilisation, the amino-group should be gradually converted into the ammonium form and the double bond of the monomer should be gradually converted into a single bond. We are thus dealing with the formation of an intermediate ylide structure †. There is at present no doubt that such structures occur as intermediates (and final) products in the reactions of acrylic esters with tertiary amines and in the condensation of nitrogen-containing heterocycles with acetylenecarboxylic acids[89]. A dipolar mechanism has been established for the reactions of acetylenecarboxylic esters with alkyl- and dialkyl-amines[86,90]. If in our case the reaction takes place via the ylide stage, this is of course because of the steric strain of the bonds and valence angles (the change of the sp^2 hybridisation of the carbon atom to sp^3 hybridisation and the conversion of the trigonal C–N–C angle into a tetrahedral angle)[91,92]. During the reaction, alkyl groups are somewhat displaced to the side opposite to that where the bulky alkylating group is introduced and there is steric interaction with the hydrogen atom of other substituents and hence repulsion. This repulsion (G. Brown's B-strain) will of course be a maximum if the reaction centre in the initial molecule is sterically hindered.

By solvating the intermediate ions, polar solvents should lower the activation energy for the reaction. In this respect, the most effective protic solvents (water, alcohols, and to some extent the excess of the amine introduced into the reaction) are capable of forming hydrogen bonds both with anions and with the ammonium ions formed ("specific solvation")[85]. Intermolecular proton migration has been demonstrated for almost all types of organic reactions catalysed by acids and (or) bases[93]. Even simple processes involving exchange between an amine and its conjugate acid and between an acid and its anion probably involve steps in which there is exchange with the medium[94]. In particular, this is why in acid-catalysed (prototropic) reactions proton transport is the rate-determining step over a definite pH range[93].

In our case the conversion of the transition complex (or the intermediate species close to it in structure) into

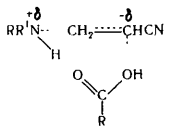
† The hypothesis of the intermediate formation of ionic species in the cyanoethylation of amines was first put forward by Timbekov and Sadykov[88].

the stable cyanoethylation product requires a double proton transfer and consequently the presence in the medium of a potential acid and base:



where B is a base and AH an acid—B and H may be part of the same molecule.

In a synchronous step of this kind[93] the bases may be the amines undergoing alkylation, other amino-components of the reaction mixture (for example reaction products, dimethylformamide, and other dialkylamides), solvent molecules when these are sufficiently basic or sterically accessible (water, alcohols), and hydroxide ions; the acids may be phenols, alcohols, water, and oxonium ions. When dipolar solvents and catalysts (ethylene glycol, organic acids) are employed, different centres of the same molecule function as acids and bases[95-97], so that the reaction complex is more compact. This can explain the higher rate of the reactions in such solvents:



In reactions with participation of metal ions (Cu^+, Cu^{2+}, Hg^{2+}) a metal ion with a vacant electron shell can serve as an acceptor for the electron pair of the CH group in the transition complex. According to some data[75], such solvation by transition metal ions may be more effective than solvation by many solvent molecules.

One can of course regard transfer processes, leading to the stabilisation of the transition state in reactions of amines with activated olefins, as reactions whose mechanism is not only of the synchronous (termolecular) type. Alcohols, water, dialkylamides, and, better still, the free amine can abstract a proton from the ammonium group and transfer it to the solution, whence it adds to the CH group[21], although energetically such a process is less favourable (retention of the charge on one side of the reaction complex). However, in both cases the solvents which show the greatest promoting effect are those which, while showing a considerable tendency towards the addition and dissociation of a proton, have molecules of small geometrical dimensions so that their incorporation in the complex or their approach to different centres of the binary ion is facilitated.

Under certain conditions, the protonation (or deprotonation) stage may compete with the primary alkylation stage as regards its importance for the overall rate of the process and to a greater extent the lower the concentration of the potential acid and the lower its donor capacity. Then the role of the base must of course be fulfilled largely by the amine undergoing alkylation. If the latter is sterically hindered or its basicity is low, both functions are carried out by the solvent (or catalyst) added. This is probably the reason for the anomalously high acceleration of the cyanoethylation of anabasine[86], 2,6-dimethylpiperidine[24], t-butylamine and related amines[21,22] following the introduction of several drops of water and acid, or dilute solutions of acid reagents. Here it is still too early to speak of changes in polarity, solvating capacity, and other macrocharacteristics of the medium. However, according to the literature, the presence of traces of proton-donor substances can strongly promote intermolecular proton transfer processes (see, for example, Giessner-Prettre and Oger[98]). On further dilution with a solvent or on further increase in the amount of catalyst, the rate of reaction increases but less appreciably and the effect is now determined by the sum of all factors. In reactions in highly dilute solutions the addition stage is of course rate-determining.

The kinetic literature data agree with the above mechanism. Cyanoethylation in aqueous or buffer solutions of ammonia[99,100], ethylamine, benzylamine, diethylamine[100], ethanolamine[78,100], amino-acids[48,50,101], and aromatic amines[69] follows second-order kinetics (or pseudo-first-order kinetics in the presence of an excess of one of the components), the non-protonated amine or the anion of the amino-acid with a free NH_2 group participating in the reaction. Therefore the pH probably affects only the concentration of the free amino-component. Thus, for amino-acids and mercapto-amino-acids, a satisfactory correlation has been found between pK_1 and pK_2 on the one hand and the kinetic characteristics of the system on the other; it is possible to estimate quantitatively the steric and polar factors with the air of a modified Hammett–Taft relation.

If one adopts as standard the rate constant for the cyanoethylation of glycine, then the following relation holds for other amino-acids: $\lg k_{A^-} = \rho\sigma^A + E_S$, where σ^A is a parameter representing the polar effect of the substituents and numerically equal to pK_2 (amino-acid) $- pK_2$ (glycine) and E_S is a steric constant, which depends on the size and the steric requirements of the substituent. Plots corresponding to substances with the amino-group at a primary, secondary, and tertiary carbon atom form separate branches with approximately the same slope ($\rho = 0.427 \pm 0.010$); their intercepts on the ordinate axis give E_S. A very sharp fall in the rate of cyanoethylation with increase of E_S (i.e. with increase in the number and bulk of substituents near the reaction centre) is typical, and has been attributed to an increase of the steric strain and steric interaction in the dipolar transition state (the telescopic effect)[50].

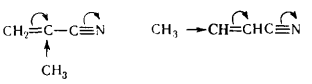
Unfortunately the kinetics of cyanoethylation in non-aqueous media have not been investigated at all[68]. To elucidate the role of proton-transfer processes, experiments in aprotic solvents with the addition of a certain amount of proton donors or acceptors would be particularly desirable.

4. SOME ANALOGUES OF ACRYLONITRILE

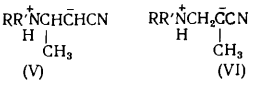
The substitution of a hydrogen atom in the acrylonitrile molecule by an alkyl group and (to a lesser extent) by an aryl group leads to decreased reactivity of the double bond in the addition reactions. Thus the nitrile of crotonic acid (or allyl cyanide, which is converted into the nitrile of crotonic acid in the presence of basic reagents) has been condensed with ammonia[102,103], methyl- and ethyl-amines[103], dimethyl- and diethyl-amines[104,105], pyrrolidine[106], ethylenimine[107], β-alanine[108], and other amino-acids[109]. As a rule these reactions take place at 70–100°C. Most of the syntheses have been carried out in dilute aqueous solutions, although the authors did not establish whether water promotes the reaction. Methods for the 2-cyanopropylation of aromatic amines (aniline, *o*- and *p*-toluidines, *o*-anisidine) are analogous to cyanoethylation methods: catalytic reaction of allyl cyanide at high temperatures in the presence of copper(I) chloride[104] and alkylation with the nitrile of crotonic acid by refluxing in

aqueous solution[105]. In both cases the yield does not rise above 10–40%. The study of the kinetics of the reaction of both isomers of crotononitrile with a number of amino-acids showed that the *cis*-compound is somewhat more reactive[101,110].

It has been established that α-substituted compounds passivate the double bond to a greater extent than substituents introduced at the β-carbon atom. Under the conditions indicated above, methacrylonitrile combines only with ethyleneimine[107], piperidine, and pyrrolidine[106] and does not alkylate diethylamine[106], benzylamine[13], aniline[105], and *p*-phenylenediamine (in the presence of acetic acid[60]). These facts are very interesting, since the +*I*-effect of the methyl group should be approximately the same in both positions[101,110].



In this connection, it has been suggested that in the transition state (VI) additional steric interactions between the CH_3 group and the substituent at the nitrogen atom are more likely than in the transition state (V)[101,107]:



(V) (VI)

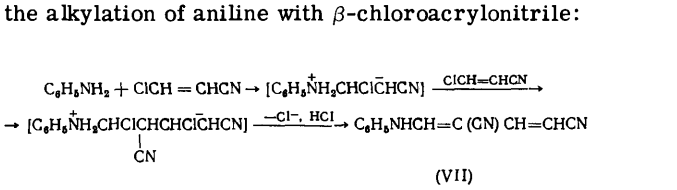
On the other hand the carbanion (V) with a negative charge at a tertiary carbon atom is apparently less stable than a similar carbanion with a negative charge at a secondary carbon atom[101].

Terent'ev and coworkers compared the relative reactivities of certain simplest αβ-unsaturated nitriles in reactions with an aqueous solution of potassium glycinate[111]. The yields of the adducts were as follows (acrylonitrile was adopted as 100): crotononitrile 23; allyl cyanide 5.3; methacrylonitrile 5; nitrile of *trans*-cinnamic acid 5; cyclohexylideneacetonitrile 8; cyclohexene-1-carbonitrile 8. Amines do not add to αβ- and ββ-dimethylacrylonitrile after prolonged refluxing both in the absence of additives and in the presence of an alkaline reagent[105,106]. 1,4-Dicyanobut-2-ene and β-cyanomethylacrylonitrile react with ammonia, various amines, and highly basic diamines at 60–70°C with formation of adducts of the type $NCCH_2CH_2CH(NRR')CH_2CN$. The addition is promoted by water as the solvent[112,113] or by 1–2% of a copper salt[114]. Dialkylamines are appreciably more active than primary amines or ammonia.

The chlorine atom is sterically similar to the methyl group but, in view of the −*I*-effect of the halogen, α-chloroacrylonitrile has a reactivity comparable with that of acrylonitrile[107,115]. If the chlorine atom is in the β-position, then in inert and even in proton-donor solvents, secondary amines are "cyanovinylated" according to the mechanism[116]:

$$ClCH{=}CHCN + RR'NH \rightarrow RR'NCH{=}CHCN$$

Similar substitution of functional groups has been noted for other classes of αβ-unsaturated compounds (β-chloroacrylates, β-halogeno- and β-alkoxy-vinyl ketones, β-chlorovinyl aryl sulphones). Nevertheless a mechanism involving initial nucleophilic addition with subsequent elimination of the hydrogen halide (or the alkoxy-group) is postulated for these reactions. In a kinetic study of the reaction of β-chloroacrylonitrile with piperidine (methanol, 0°C) appreciable differences between the rates for the *cis*- and *trans*-isomers were not observed (K_2 was respectively 2×10^{-2} and 2.67×10^{-2} litre mole^{-1} s^{-1}). Sterically homogeneous *trans*-2-piperidinoacrylonitrile was formed in both cases[116] (cf. ethyl β-chloroacrylate[117]). According to the authors[116], the intermediate dipolar ion has an appreciable lifetime, which permits isomerisation by rotation about the C–C bond. These views are indirectly confirmed by the formation of the bisadduct (VII) in the alkylation of aniline with β-chloroacrylonitrile:



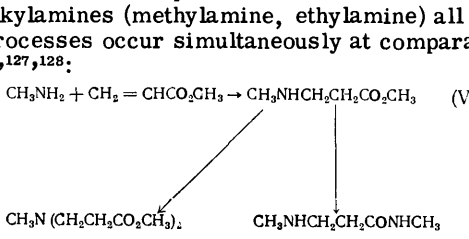
(VII)

5. ACRYLIC ACID ESTERS

Highly basic heterocyclic imines—ethyleneimine[107], pyrrolidine, piperidine[119,120], morpholine[16], and hexamethyleneimine[121]—readily add to the double bond ‡ of methyl and ethyl acrylates, sometimes with a slight temperature rise, giving high yields of the corresponding esters of *N*-substituted aminopropionic acids. The reaction of lower dialkylamines is slower[120,122]. Even the reaction of dibutylamine requires a long time[120,123], probably due to the high steric hindrance at the nitrogen atom.

Similarly, 2-methylaminobutane (with an imino-group at a secondary carbon atom) reacts with ethyl acrylate only when the mixture is refluxed, and di-isopropylamine and di-s-butylamine do not react even on prolonged refluxing with ethyl acrylate[119,124]. However, recently it proved possible to carry out the addition of di-isopropylamine and 2,6-dimethylpiperidine to methyl acrylate in methanol[121].

The interaction of ammonia and primary amines with acrylic acid esters both without solvent and in methanol can take place in three ways. The weakening of the basicity of the alkylamine caused by the introduction of the group $CH_2CH_2CO_2R$ is relatively slight (see, for example, Holley and Holley[125]), so that the initially formed monoadduct can combine with a second molecule of acrylate. Furthermore, the addition reaction may be accompanied by the conversion of the ester group into an amide group, at least at elevated temperatures. Thus in the case of lower alkylamines (methylamine, ethylamine) all the above processes occur simultaneously at comparable rates[122,127,128]:



(VIII)

The yield of the amide then increases in proportion to the duration of the experiment. The formation of the monoadduct (VIII) appears to be favoured by the replacement of

‡ The same applies also to butyl, allyl, and other alkyl esters of acrylic acid, which are much more rarely used in chemical practice. It has been established that the amine may attack the C–O bond in cyanomethyl and *p*-nitrophenyl esters of αβ-unsaturated acids with formation of acid amides[18].

methanol by ethanol. As might have been expected, the reaction does not occur when ethylamine is introduced as the hydrochloride [129].

For less basic amines (butylamine, cyclohexylamine, β-tetrahydronaphthylamine, benzylamine, α-methylphenylethylamine), the formation of mono-2-alkoxycarbonylethyl derivatives takes place fairly smoothly in the mixture with acrylate kept in methanol for a period ranging from one day to several weeks [129-134]. Primary amines with tertiary substituents (t-butylamine, t-octylamine, 2-amino-1-ethoxycarbonyl-2-methylpropane) add to acrylic acid esters only under very severe conditions [20,130]. To accelerate the process, the latter is carried out in aqueous solution in the presence of alcohol or dilute acid [22,25,131,135]. According to patent data [136], acetic acid effectively catalyses the reactions of acrylates also with other strongly sterically hindered amines such as di(2-ethylhexyl)amine §. It is suggested that certain alkaline reagents be used as catalysts for the reactions of polymethyleneimines [107,138], but these data require verification.

In contrast to the cyanoethylation reaction, when aliphatic and aliphatic-aromatic primary amines are simply refluxed with 2–3 moles of acrylate, high yields of bisalkoxycarbonylethylation products are obtained [124,135,139]. According to other data, the latter reactions take place satisfactorily at lower temperatures too in alcoholic media [130]. This also applies to the addition of methyl and ethyl acrylates to amino-esters with the general formulae (IX) [139,140] and (X) [123,141,142]:

$$C_6H_5(CH_2)_n NHCH_2CHRCO_2R' \qquad RNHCH_2CHR'CO_2R^2$$
(IX) (X)

It is interesting that the shift of the branching point of the alkyl chain towards the nitrogen atom, which hinders the usual addition of acrylates, stimulates the "symmetrisation" reaction [142-144]:

$$C_6H_5(CH_2)_2NHCHCH_3CH_2CO_2C_2H_5 \xrightarrow{\vee\,/\,\wedge} C_6H_5(CH_2)_3NCHCH_3CH_2CO_2C_2H_5$$
$$\rightarrow C_6H_5(CH_2)_2N(CH_2CH_2CO_2CH_3)_2 \qquad CH_2CH_2CO_2CH_3.$$

Methyl and ethyl acrylates can react, albeit with difficulty, with aniline in the presence of alkaline catalysts or methanol [145,146], but the yield of adducts is low. For preparative purposes, the 2-alkoxycarbonylethylation of aromatic amines is carried out with heating (8–15 h) in the presence of acetic acid [147]:

$$ArNH_2 + CH_2{=}CHCO_2R \xrightarrow{H^+} ArNHCH_2CH_2CO_2R$$

The reactions of methyl acrylate with aniline [38,148-150], toluidines [132-150], anisidines [148,149], halogenoanilines [132,148], *N*-alkylanilines, and α-naphthylamine and its analogues [150,151] have been achieved under these conditions. Amines of low basicity (diphenylamine, *o*-, *m*-, and *p*-aminobenzoic acids [151-153]) require more prolonged heating. Acetic acid can be replaced by acetic anhydride or an ammonium salt [120]. It has been stated that anhydrous stannous chloride has a catalytic effect [129,148].

A number of studies have been made on the kinetics of the reaction of amines with acrylic acid esters [48,77,101,145,154]. The reactions of morpholine and piperidine with acrylates in methanol are of second order, are not inhibited by alkalis, but are somewhat inhibited in the presence of acid reagents (acetic or perchloric acid). Replacement of part of the methanol by benzene greatly reduces the rate of the process, the rate decreasing faster than the dielectric constant of the mixture. The reactivity of methyl acrylate is higher than that of ethyl acrylate, but the latter scarcely differs from that of the butyl ester.

Table 1 lists the rate constants for the pseudounimolecular reaction of methyl acrylates with various amines in tetrahydrofuran (THF) [145].

It is striking that ethanolamine reacts 150 times faster than allylamine which has the same pK_a and ten times faster than the highly basic butylamine. A similar anomaly has been noted also for the diethanolamine–benzylamine pair. The reactivity of amino-alcohols $HO(CH_2)_nNH_2$ is almost independent of the number of methylene groups n, [154] and therefore in all cases it is necessary to assume an accelerating effect of the HO group, probably as a result of intermolecular interactions.

Table 1.

Amine	pK_a	K_1^{20}, min^{-1}
Ethanolamine	9.50	$2.4 \cdot 10^{-2}$
Butylamine	10.59	$2.1 \cdot 10^{-3}$
Allylamine	9.49	$1.6 \cdot 10^{-4}$
Diethanolamine	8.80	$9 \cdot 10^{-5}$
Benzylamine	9.34	$5 \cdot 10^{-5}$

Indeed when the reaction of ethanolamine with methyl acrylate is carried out at 20°C in dioxan, pyridine, dimethylformamide, and acetonitrile, a very slight increase of k_1 (from 2×10^{-2} to 4×10^{-2} min^{-1}), corresponding to the increase in the polarity of the medium, was observed [145]. However, in methanol, which has a smaller dielectric constant but is a potential proton donor, $k_1 = 9 \times 10^{-2}$ min^{-1}. (The high value $k_1 = 7 \times 10^{-2}$ min^{-1} quoted for the reaction in tetrahydrofuran may be due to the effect of peroxy-compounds [155]). Similarly it has been shown that the condensation of butyl-amine with ethyl acrylate in tetrahydrofuran [154] is very markedly accelerated (by a factor of 5–350) on introduction of alcohols, water, and butanethiol. These findings agree well with the hypothesis that the reactions of amines and activated olefins have the ionic mechanism discussed above for acrylonitrile [29].

A group of American workers [48,101] compared the reactivities of vinyl compounds of the acrylic series in reactions with 11 amino-acids. At pH 8.5 (30°C) methyl acrylate proved to be 3.6 times more reactive in relation to glycine than acrylonitrile. This is somewhat inconsistent with other observations [6,8] according to which the nitrile group has more pronounced electron-acceptor properties than the ester group. To account for this fact, it was suggested [101] that, in condensation with neutral nucleophilic reagents, one of the additional factors determining the reactivity of the olefins $CH_2{=}CHX$ is resonance stabilisation of the transition state by the functional group X. This is of course more likely for $COOCH_3$ than for CN.

There are few data for the reactions of alkylacrylic acid esters with amines. The introduction of a methyl substituent at the double bond of methyl acrylate has little effect on the bond polarity, but, as in the case of acrylonitrile, it significantly reduces the steric accessibility of the reaction centre. The relative rates of reaction of methyl *trans*-crotonate and methyl methacrylate with glycine in aqueous buffer solutions are respectively 0.24 and 0.0116 of the rate of cyanoethylation of glycine [101].

§ In reactions with participation of acrylic and methacrylic esters in an aqueous medium, an anomalous reaction involving the migration of alkyl groups may take place to some extent as well as the addition of amines to the double bond [137].

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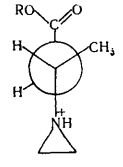
It is interesting that crotonates exhibit more stringent steric requirements as regards the structure of the amine. Thus ethyl crotonate combines with piperidine [156], dimethylamine [157], propylamine [124], and methylamine [156,158] only on refluxing. In the last case variable amounts of the *N*-methylamide of 3-methylaminobutyric acid are also formed [158]. Diethylamine scarcely reacts with ethyl crotonate without heating, while at 200°C the main product is *N*-ethylcrotonamide. Normal, albeit slow, addition to the double bond occurs only in alcoholic solution [158]. On the other hand, the condensation of ethyl crotonate with butyl-, cyclohexyl-, benzyl-, and phenylethyl-amines takes place in alcohol even at room temperature [143,159,160], high yields of monoalkylation products being achieved.

Another unexpected observation of the steric inhibition of the reaction was made in a comparative study of the condensation of ethyleneimine with methyl and ethyl crotonates [107]. At 75°C methyl crotonate reacts completely, while its homologue gave only 2% of the adduct. Probably this is due to the mutual repulsion of the methyl and ester groups in the transition state (Newman's projection), which increases sharply with increasing size of the substituent R.



p-Anisidine and *p*-chloroaniline add to ethyl crotonate on refluxing in the presence of small amounts of acetic acid [161]. Ethyl and methyl ββ-dimethylacrylates combine slowly with methylamine [162] and very slowly with ammonia [156] in alcoholic solutions. On heating with anhydrous ethylamine, the main product is the *N*-methylamide; in the absence of additives, there is no reaction with piperidine [156]. Dimethylamine condenses with the β-dimethylaminoethyl ester of ββ-dimethylacrylic acid in the presence of acetic acid [163].

Methyl methacrylate readily reacts with piperidine [164], but the reaction with dimethyl- and diethyl-amines requires prolonged heating [44,124]. As already mentioned above, the ethyl ester proved to be even less reactive under comparable conditions [153,157]. Non-catalytic reactions of methacrylates with a number of aliphatic and aliphatic-aromatic amines have also been described [124,140,165]. However, the addition of methyl methacrylate, on refluxing the mixture, to dibutylamine [123], ethyl *N*-methylaminopropionate [123,141], and t-butylamine [166] could not be achieved. Aniline reacts with methyl methacrylate at 200°C to give a low yield of a mixture of three substances: the normal addition product, the anilide of 3-anilino-2-methylpropionic acid, and methacrylanilinide [120].

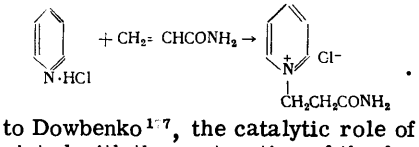
When alcohols are used as solvents, the reaction is either initiated or the temperature required is appreciably reduced. Thus in the presence of methanol the reactions of lower amines and dialkylamines (and also benzylamine) give, after a fairly long time, high yields of the corresponding monoadducts even at a low temperature [123,127,128,137,142,160,164]. With methylamine, a small amount of the double addition product is also obtained [123]. Hexamethyleneimine, β-tetrahydronaphthylamine, and cyclohexylamine react with methyl methacrylate on heating in the presence of added alcohol—the reaction takes place smoothly without the formation of side products [121,167]. For aniline, it is recommended that the synthesis be carried out in the presence of acetic acid [44,164], while methanol is inactive as a catalyst [120]. Acid catalysis can probably be used also in the reactions of other weakly basic amines, for example carboline derivatives [168].

The ethyl ester of α-ethylacrylic acid does not react with ammonia and dimethylamine on prolonged heating [156]. However, in an alcoholic medium it proved possible to add methyl-, butyl-, and benzyl-amines to a number of α-alkylacrylates with high yields [140,169].

6. ACRYLAMIDE

Diethylamine adds to acrylamide on refluxing (2–3 h), while without heating the reaction scarcely occurs [170]. It has been stated that with ammonia there is a possibility of the formation of a bis- or even a tris-adduct [171,172]. When acrylamide is added to an alcoholic solution of piperidine and morpholine, the process begins exothermically [121,170,173], although heat is required to complete the reaction. The method of 2-carbamoylethylation in alcoholic media has been successfully applied to dimethyl-, dipropyl-, and dibutyl-amines [173] and to a number of ring-substituted benzylamines [121,165,174]. For amines of low basicity (pyrazolines, pyrazoles, amino-acids), aqueous solutions are employed, sometimes with the addition of tertiary amines [108,121,172,175]. The effect of solvents on the addition of acrylamide to an amino-group proved to be more pronounced than in the case of acrylonitrile [29,121,165], but the overall nature of the catalysis by proton-donor solvents is probably the same. In particular 3-arylaminopropionamides may be obtained by condensing substituted anilines with acrylamides in the presence of both water and acetic acid in alcohol [147,176]. The kinetics of 3-carbamoylethylation of amino-acids have also been described [48,101].

Acrylamide can combine with the hydrochloride of pyridine (and a number of other heterocyclic bases) on refluxing in methanol [177]:



According to Dowbenko [177], the catalytic role of the acid is not associated with the protonation of the functional group of acrylamide.

N-Dodecylacrylamide (and dodecyl acrylate) reacts slowly by a similar mechanism with trimethylammonium and pyridinium salts [178]. Triethylamine proved to be inactive, probably for steric reasons or because of the impossibility of charge delocalisation of the type which occurs in pyridinium salts.

The substitution of hydrogen atoms in the amide group of acrylamide by alkyl groups alters the reactivity of the double bond but not always in the same way [8,107,179]. Thus *N*-benzylacrylamide reacts smoothly on heating with hydrazine hydrate in the presence of alcohol and dimethylformamide [180]:

$$N_2H_4 \cdot H_2O + CH_2{=}CHCONHCH_2C_6H_5 \rightarrow NH_2NHCH_2CH_2CONHCH_2C_6H_5 .$$

With phenoxycarbonylhydrazine, similar condensation takes place on refluxing with added acetic acid [181]. The reactions of *N*-methyl-, *N*-benzyl-, and *NN*-dimethylacrylamides with the most basic aromatic amines, which occur relatively readily in the presence of organic acids, have been described [182].

Diacrylamidomethane and 1,3,5-triacryloyl-1,3,5-triazine react similarly [183,184]. In the condensation of bisacrylamides (particularly 1,4-diacryloylpiperazine) with

primary and secondary amines in proton-donor media, polymers were obtained [185]. The reactions of α- and β-methyl-acrylamides have been described [172,186,187].

7. ACRYLIC ACID

Acrylic acid itself and its alkyl-substituted derivatives are the least reactive among acrylic olefins in condensations with amino-compounds. Thus aqueous ammonia (in a large excess) adds to crotonic and $\beta\beta$-dimethyl-acrylic acids after prolonged heating in an autoclave [188]. The same reaction involving crotonic acid takes place more readily on irradiation with ultraviolet light, the product being N-methyl-β-alanine and also its amide [189].

One of the factors inhibiting the reactions of acrylic acids with amines is undoubtedly salt formation and the consequent decrease of the activating effect of the carboxylate group on the adjacent double bond. Thus when crotonic acid is mixed in alcohol with 2-aminoethanol, 2-hydroxyethylammonium crotonate is precipitated [190]. After heating to 100°C, the latter is converted into β-(2-hydroxyethylamino)butyric acid.

Recently several ways have been suggested for overcoming these difficulties. For example, benzylamine, some of its substituted derivatives, isobutylamine, and hexylamine have been added to crotonic acid with high yields on heating an equimolar mixture of the reactants in pyridine solution [134,191,192]; when optically active α-phenylethylamine is introduced into this reaction, a mixture of diastereoisomers is formed, which can be separated [193]. The use of proton-donor solvents (water, lower alcohols, ethylene glycol) has been recommended in patents [194,195] for the synthesis of the adducts of unsaturated acids with higher aliphatic amines and polyamines. Nevertheless in a few cases the reaction in aqueous solution takes place in different ways and polymeric substances are formed together with alkylaminopropionic acids. Probably this can be explained by the addition of the monomer to the intermediate ion (XI) [192]:

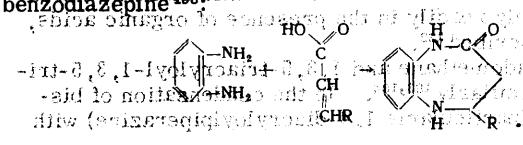
$$RNH_2 + CH_2=C(CH_3)CO_2H \rightarrow R\overset{+}{N}H_2CH_2\overset{-}{C}(CH_3)CO_2H\ .$$

Acrylic and methacrylic acids interact with an excess of aniline only at 180–190°C, the reaction involving both the double bond and the carboxy-group [196]:

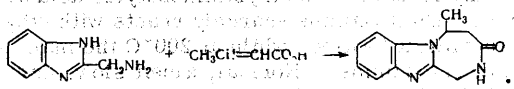
$$C_6H_5NH_2 + CH_2=CHCO_2H \rightarrow C_6H_5NHCH_2CH_2CONHC_6H_5\ .$$

Adducts of aromatic amines and $\alpha\beta$-unsaturated acids (1 : 1 composition) can be obtained in a low yield by exposing toluene solutions of the reactants to ultraviolet light [188]. Equivalent amounts of p-chloroaniline and crotonic acid were successfully condensed on refluxing in benzene [161]. According to the authors [161], in this case crotonic acid behaves at the same time as an acid catalyst. In a 1937 patent application by I.G. Farbenindustrie [197] the adducts of acrylic acid with a number of aromatic amines were described, but these data have not been reproduced so far.

The condensation of $\alpha\beta$-unsaturated acids and also their esters with difunctional amines leads to the formation of seven-membered heterocyclic compounds. For example, o-phenylenediamine is converted into the corresponding benzodiazepine [198]:



The structure of products of similar condensations is determined both by the reaction conditions and the relative nucleophilicity of the functional groups. When 2-aminomethylbenzimidazole is heated with crotonic acid, the double bond attacks a ring nitrogen atom [199]:



When the molecule contains a mercapto-group (o-aminothiophenol, β-aminoethanethiols), the reaction takes place with initial 2-carboxyethylation of the sulphur atom [200].

8. VINYL KETONES

Vinylketones (CH_2=CHCOR) have a highly activated double bond and their reactions with aliphatic dialkylamines and heterocyclic imines take place very vigorously [107,201–203]:

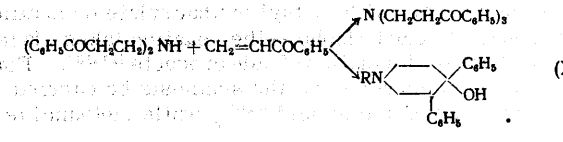
$$RR'NH + CH_2=CHCOR^3 \rightarrow RR'NCH_2CH_2COR^3\ .$$

Therefore the reaction is usually carried out either with cooling [204] or in ethereal and benzene solutions; in some cases alcohols have also been used as solvents [205].

When the rate of reaction is high, it is difficult to estimate qualitatively the effect of the basicity of the amino-component [204]; on the other hand, the effect of steric factors is very distinct. Thus a very bulky substituent in the 2-position of the piperidine ring (or two small substituents) greatly hinders the reactions with aryl vinyl ketones. Whereas dimethyl- and diethyl-amines react quantitatively with methyl vinyl ketone even at −5°C, the preparation of the corresponding adducts of methylcyclopentyl- and methylcyclohexyl-amines requires heating to 40°C [204]; the reaction of di-isopropylamine and dicyclohexylamine with methyl vinyl ketone would not proceed at all. The relative decrease of the rate of reaction is characteristic also of 2-alkylcarbonylethylation of amines with low basicity [206].

Primary aliphatic amines usually react with vinyl ketones without solvent, a complex mixture of products being formed (probably because of the simultaneous attack on the double bond and the carbonyl group). The process can be regulated by adding acetic or formic acid to the reaction mixture, so as to bind part of the amine [202]. Under these conditions, propylamine with ethyl vinyl ketone yields a mixture of mono- and di-adducts. Likewise, while aqueous ammonia and vinyl ketones form a mixture of di- and tri-alkylation products [207], with ammonium acetate it is possible to obtain a small amount of the monoadduct [201]. However, there are data [208,209] showing that ammonia and methylamine in the form of their hydrochlorides do not react with phenyl vinyl ketone even on heating in aqueous alcohol. In another method the monoadducts of primary amines and methyl vinyl ketone are synthesised at room temperature or with cooling in ethereal solution [210].

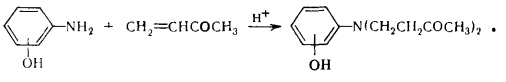
By heating an aqueous alcoholic solution of β-benzoylethylamine with phenyl vinyl ketone, the triadduct $N(CH_2CH_2COC_6H_5)_3$ was obtained, while the reaction of di(benzoylethyl)amine with the same unsaturated ketone yields a mixture of the same triadduct and a piperidinol (XII, R' = $C_6H_5COCH_2CH_2$) [208,209]:



On the other hand, the hydrochloride of *N*-benzoylethyl-*N*-methylamine and phenyl vinyl ketone form the adduct $(C_6H_5COCH_2CH_2)_2NCH_3$ or its mixture with a piperidinol of type (XII), with R = CH_3, depending on the medium (water or aqueous alcohol). Probably in both cases the reaction proceeds via a dipolar intermediate state, which is stabilised by the addition of a proton or by intramolecular aldol condensation[208].

Aromatic amines (aniline, *p*-toluidine, certain *N*-alkylanilines) add to methyl vinyl ketone[210,211], ethyl vinyl ketone[211,212], phenyl vinyl ketone[213-215] on slight heating or standing for a long time at room temperature. It has actually been stated that the addition of aniline to phenyl vinyl ketone causes an exothermic reaction[214], but the less basic anthranilic acid gives high yields only at 60°C[216]. The addition of an unsaturated ketone to an aromatic amine is the first stage in the synthesis of quinolines by the Döbner–Miller method[217]. In the presence of a proton-donor solvent (methanol, 50% ethanol) these processes appear to be accelerated[215,216]. When *N*-methylaniline and dimethylamine hydrochlorides are introduced into the reaction under these conditions, a mixture of Mannich bases is formed from both amines as a result of a mobile equilibrium[215]. The addition of an inert solvent appears to inhibit 2-carbonylalkylation of amines[216].

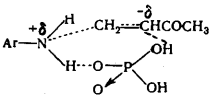
The products of the addition of methyl vinyl ketone to *p*-phenylenediamine and its analogues have been described[216]. In methanol in the presence of a slight excess of the unsaturated component, a bismonadduct is formed, while refluxing with an excess of methyl vinyl ketone leads to double alkylation of both amino-groups. When an acid catalyst (acetic acid) is used, it is also possible to obtain dialkylation products of other, somewhat less basic aromatic amines but there are few such examples yet[218]:



The study of the kinetics of the addition reactions has shown[101] that in aqueous solutions methyl vinyl ketone reacts with glycine eighty times faster than does acrylonitrile. Zuman and coworkers[219,220] determined polarographically the first-order rate constant for the reaction of phenyl vinyl ketone with a tenfold excess of morpholine and a number of primary amines in the presence of the corresponding hydrochlorides. The reaction with ethanolamine and cyclohexylamine goes almost to completion, while for other amines an equilibrium was observed after 37–60% conversion. Within the limits of experimental error, k_1 proved to be independent of ionic strength and pH. A direct correlation between the rate of 2-phenylcarbonylethylation and the basicity of the amine has not been found and therefore the different values of k_1 have been attributed mainly to the effect of steric factors[101]. This interesting result has not been adequately explained.

The reaction of methyl vinyl ketone with aromatic amines (in an acetate or phosphate buffer solution) up to a conversion in excess of 80% is satisfactorily described by a second-order equation[210]. The Hammett equation with $\rho = -1.60$ holds ($r = 0.998$; $s = 0.09$) for p-$RC_6H_4NH_2$ (R = CH_3O, CH_3, H, Cl, NO_2). The activation energy for the reaction in the temperature range 20–50°C is 5.2–6.1 kcal mole^{-1} and the entropy is between −48 and −50 e.u. By varying the composition of the buffer solution and its concentration, the authors established that the process is catalysed by both acids and bases (Table 2).

The activity of the $H_2PO_4^-$ ion is striking; it greatly exceeds the catalytic effect of acetic acid which has a much higher pK_a value. The phosphate ion may be involved in the transition state as a bifunctional catalyst:



If the reaction is carried out in dioxan–water mixtures, the catalytic effect of aniline itself (and similarly pyridine) is clearly shown. Evidently the amino-component in some form can participate in the formation of the transition complex, functioning, together with water, as a proton-transfer agent.

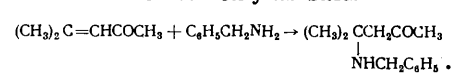
Table 2. Catalytic constants (k_1) for the reaction of methyl vinyl ketone with aniline at 31°C under different conditions.

Catalyst	Water	Solvent (40% aqueous dioxan)	Catalyst	Water	Solvent (40% aqueous dioxan)
CH_3COOH	0.02	—	H^+	10^3	
CH_3COO^-	0.26	—	Water	$5.5\cdot10^{-3}$	$1.6\cdot10^{-4}$
$H_2PO_4^-$	0.45	—	Aniline	—	$4.3\cdot10^{-3}$
HPO_4^{2-}	0.42		Pyridine	—	$7\cdot10^{-2}$

Alkyl substituents at the double bond of vinyl ketones (usually a methyl group) lower its reactivity only slightly. Thus the ketones RCOCH=$CHCH_3$, where R = methyl, phenyl, or alkoxyphenyl, combine with aliphatic amines, piperidines, and morpholine at room temperature[221,222]. High yields of monoalkylation products are attained after 1–4 h if the reaction is carried out in methanol or water.

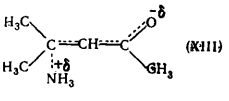
α-Benzylidene-ketones react with secondary amines somewhat more slowly[223] and the reaction depends more on steric factors than on the basicity of the amine. For example, diethylamine already adds with difficulty to methyl styryl ketone.

Among multiply substituted vinyl ketones, the condensations of amines with mesityl oxide has been most thoroughly investigated[224]. In the presence of water mesityl oxide combines with ammonia, methylamine, benzylamine, and hydroxylamine and its *N*-alkyl derivatives. However, the adducts formed are thermally unstable and can be isolated only as salts:



Diethylamine adds to mesityl oxide without solvent at 50°C[225]. Aromatic amines react with difficulty and do not give high yields. Mesityl oxide and other vinyl ketones react with diamines and amino-thiols forming seven-membered heterocyclic nitrogen-containing compounds[198].

On the basis of the study of the kinetics of the reaction of mesityl oxide with ammonia under pressure in aqueous solution or in methanol[226], the intermediate formation of the dipolar ion (XIII) has been suggested:



(XIII)

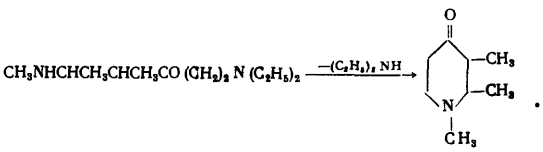
The rate of reaction in methanol increases with pressure appreciably faster [$\ln(k_p/k_1) = 1.224$] than in water (0.737) but nevertheless remains lower by a factor of 3–5. Calculation based on activation volumes shows a considerable

separation of charges in the transition state (0.42–0.65 of electron charge).

Compounds of the type $R_2C{=}CHCOCH{=}CH_2$, where one vinyl group is markedly screened, undergo smooth addition of aliphatic dialkylamines, piperidine, isopropylamine, and aniline to the sterically accessible double bond on brief heating to 60°C [207]. The yields fall somewhat with increasing length of the alkyl group R. The reaction with isopropylamine is accelerated by the addition of a few drops of water:

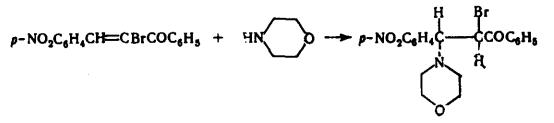
$$(CH_3)_2C{=}CHCOCH{=}CH_2 + (CH_3)_2CHNH_2 \rightarrow (CH_3)_2C{=}CHCO(CH_2)_2NHCH(CH_3)_2 .$$

In an alcoholic or aqueous medium it is possible to achieve a condensation involving the second double bond as well. Thus 1-diethylamino-4-methylhex-4-en-3-one combines with methylamine and certain other primary amines, forming a linear diadduct [228]. However, on heating these reactions lead to cyclisation with formation of γ-piperidones [228,229]:

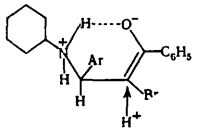


It is possible to use directly mixtures of a primary amine with divinyl ketones or β-methoxyalkyl vinyl ketones [230]. The cyclisation reaction, which consists essentially in a dialkylation process involving the amino-group, is of course controlled both by steric factors and by basicity [228,230,231]. A large number of γ-piperidones with various substituents in the ring and at the nitrogen atom have been obtained by this process.

A number of studies dealing with the stereochemistry of the addition of amines to the double bond of $\alpha\beta$-unsaturated ketones have been published. In the condensation of morpholine in benzene with *cis*- and *trans*-isomers of α-bromo-4-nitrochalcone, the same sterically homogeneous *threo*-adducts were obtained regardless of the configuration of the ketone, although the yield was somewhat higher when the *trans*-isomer was used [223]:



Primary amines (for example cyclohexylamine) react with α-bromochalcones forming diastereoisomeric β-amino-α-bromo-ketones, which cyclise spontaneously during the reaction, with retention of the configuration, to the corresponding *cis*- and *trans*-ethyleneimines [233,234]. It was found that the ratio of the isomers, as in the case of heterocyclic imines, is almost independent of the configuration of the initial $\alpha\beta$-unsaturated ketone, but may vary with the solvent. From these data, it was concluded [232,234] that the alkylation reaction proceeds via an intermediate complex incorporating the enolic form of the ketone:



The protonation of the α-carbon atom by the bulky cyclohexylammonium ion (in inert media) is responsible for the preferential formation of *trans*-adducts. Methanol probably attacks the complex less specifically, which results in an increase of the yield of products with a *cis*-configuration. These results have been analysed in greater detail by Hughes [23].

9. NITRO-OLEFINS

In a discussion of reactions involving a double bond activated by an adjacent nitro-group, it is necessary to take into account not only the polarity of the bond [5,6] but probably also the greater possibility of the delocalisation of a negative charge in the activated complex. On the other hand, the properties of nitro-compounds as carbon acids play a certain role, so that sometimes the process may occur autocatalytically. This is the reason for the exceptional ease of the reaction, of even highly substituted nitro-olefins, with nucleophilic reagents, including amines.

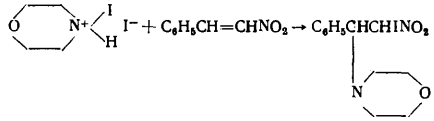
A typical example is provided by nitroethylene [236,237]. In an inert solvent (ether, dioxan, xylene, nitrobenzene) it combines with benzylamine, cyclohexylamine, and *N*-methylcyclohexylamine even at −20°C with formation of the corresponding 2-nitroalkylamines. Under the same conditions, benzylamine gives with an excess of the olefin the diadduct $C_6H_5CH_2N(CH_2CH_2NO_2)_2$. Two adducts (1 : 1 and 1 : 2) can also be obtained from aniline at 20° and 40°C respectively [236–238]. On slight heating, naphthylamines, *N*-alkylanilines, aminoanthraquinones, and aromatic diamines are 2-nitroethylated [227].

Homologues of nitroethylene combine with ammonia, diethylamine, and aromatic amines at room temperature without solvent or in ethereal solution [238]. Because of their instability, the acids are usually isolated as salts. The nitro-olefin $CH_3OCOCH_2[CH(OCOCH_3)]_3CH{=}CHNO_2$ has been successfully condensed (in the presence of methanol) with ammonia, benzylamine, cycloalkyleneimines, 2-aminoethanol, and isopropylamine. Under comparable conditions, aromatic amines give lower yields [239].

Under mild conditions, ω-nitrostyrene combines with piperidine, ammonia, semicarbazide, aniline, phenylhydrazine, benzidine, and a number of other amines [238,240]. Probably the yield of adducts is determined mainly by the isolation conditions and cannot be related to the basicity of the amine used. Thus with *p*-toluidine the reaction is completed after several minutes. Nevertheless aromatic amines of low basicity (for example, *p*-chloro- and *p*-nitro-anilines) do not react with ω-nitrostyrene at room temperature. Condensations of this kind are usually not carried out with heating to avoid secondary reactions. For example, it has been shown that certain 1-aryl-2-nitroethylation products are cleaved at elevated temperatures with formation of nitromethane [241]:

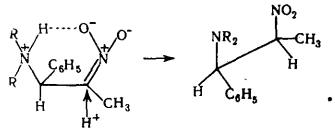
$$C_6H_5NHNH_2 + ArCH{=}CHNO_2 \rightarrow C_6H_5NHNHCHArCH_2NO_2 \rightarrow C_6H_5NHN{=}CHAr + CH_3NO_2 .$$

The addition of hydrazine and a number of acylhydrazines to ω-nitrostyrene has been achieved in absolute alcohol [242]. When the iodonium complex of morpholine is introduced into the condensation reaction in the presence of acetic acid, a positively charged iodine atom enters into the molecule of the alkylation product [243]:



The reactions of β-methyl-β-nitrostyrene with pyrrolidine, piperidine, morpholine, and certain aliphatic

amines have been investigated stereochemically[244]. In petroleum ether with equimolar proportions of the reactants, the *erythro*-isomers are formed preferentially while in the presence of an excess of the amine or in an alcoholic medium the main products are the corresponding *threo*-isomers. It was assumed[244] that the reaction takes place via an intermediate *aci*-compound, which exists as the inner complex (XIV):



(XIV)

The proton donor should attack it preferentially from the unhindered side, which leads to the *erythro*-disposition of the substituents. The gradual isomerisation of the *erythro*-isomers gives the more stable *threo*-adducts.

A number of studies have been made to elucidate the effect of substituents in the aromatic ring on the reactivity of arylnitro-alkenes. Methyl, methoxy-, or hydroxy-groups in the para-position of the benzene ring occasionally deactivate the double bond and the corresponding nitro-olefins cannot be condensed with *p*-toluidine and *p*-phenylenediamine (slight heating in the presence of alcohol)[245,246]. The introduction of an additional nitro-group or halogen atom leads, on the other hand, to an increase of the electrophilicity of the double bond[245-247]. Thus 2-chloro-4-nitro-ω-nitrostyrene readily reacts with many aromatic amines and hydrazines[247].

The nitro-group in the *ortho*- or *para*-position relative to the double bond of the styrene molecule activates the latter sufficiently for certain nucleophilic reactions[248]. On being refluxed in alcoholic solutions with an excess of secondary amines (pyrrolidine, piperidine, dimethylamine), *p*-nitrostyrene forms the corresponding adducts in yields in excess of 90%; the yield gradually falls on going to diethyl- and dipropyl-amines. When di-isopropylamine is used, only traces of the desired product are obtained, and di-isobutylamine does not react with *p*-nitrostyrene at all. In all cases *o*-nitrostyrene is less reactive. t-Butylamine reacts with difficulty with *p*-nitrostyrene and in particular with *o*-nitrostyrene (yields 45 and 7% respectively). It has been shown that these effects are not associated with the interaction between the amines and the nitro-group but are caused by direct frontal hindrance of the addition reaction.

Recently very interesting results were obtained in the study of the kinetics of the reaction of butylamine and benzylamine in dioxan with various nitrostyrenes, β-nitropropenylbenzenes and β-nitrobutenylbenzenes[249]. The pseudo-first-order constants obtained can be represented by the equation

$$K_{tot} = [RNH_2]^2/[A(RNH_2] + B)$$

where A and B are constants which can be roughly correlated with Hammett's σ coefficients. In other words, the authors believe that the transition state of the reaction includes, together with the αβ-unsaturated compound, two molecules of the amine. On the other hand, if the condensation (for example with aniline) is carried out in an alcoholic solution of a phosphate buffer, the reaction is of first order with respect to the amino-component. Consequently in such cases the protic solvent assumes the functions of the second amine molecule.

10. VINYL SULPHONES

The available information about the condensation of vinyl sulphones with nucleophilic reagents is insufficiently systematic[6]. For a long time the problem of the nature of the interaction between the double bond and the sulphonyl group also remained unresolved[250,251]; it is most reasonable to assume a purely inductive effect of the SO_2R group. This makes even more unexpected the appreciable reactivity of vinyl sulphones in reactions with amino-compounds[101].

Aryl vinyl sulphones have been thoroughly investigated in this respect, particularly the readily available p-$CH_3C_6H_4SO_2$-$CH{=}CH_2$ [252-255]. The latter sulphone gives quantitative yields of adducts with various amines in benzene solution at room temperature[256,257]. However, the addition of sterically hindered amines such as diazopropylamine could not be achieved[256]. In preparative experiments methanol as solvent has a favourable effect[254,255]. Condensations involving allyl aryl sulphones, which are evidently first isomerised to the αβ-unsaturated isomers, also take place comparatively readily at 50–70°C [255,258]:

$$ArSO_2CH_2CH{=}CH_2 + R_2NH \rightarrow ArSO_2CH_2CH(CH_3)NR_2 .$$

Table 3. First-order rate constants for the reaction of *p*-tolyl vinyl sulphone with amines in alcohol at 25°C.

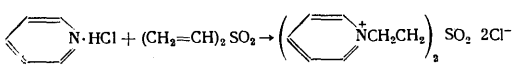
Amine	pK_a	$k_1 \cdot 10^3$	Amine	pK_a	$k_1 \cdot 10^3$
Piperidine	11.1	585	Hexylamine	10.6	10.6
Dimethylamine	10.8	451	Butylamine	10.6	8.0
Morpholine	8.4	33.8	Isopropylamine	10.6	4.32
Diethylamine	11.0	23.3	s-Butylamine	10.6	4.24
Dibutylamine	11.3	12.5	2-Ethylpiperidine	—	3.78
2-Methylpiperidine	11.0	10.9	t-Butylamine	10.7	0.86
Isobutylamine	10.7	10.8	2,6-Dimethylpiperidine	11.1	0.085

The addition of numerous amines of different classes to the double bond of aryl vinyl sulphones was recently investigated by kinetic methods[256,257,259]. It was found that, as in the case of vinyl ketones, the reactivity of the amines depends more on the steric environment of the nitrogen atom than on its basicity[256] (Table 3). In alcohol the reaction is definitely of first order with respect to each component; in benzene solution the rates of all the reactions are greatly reduced (approximately by a factor of 40) and the order with respect to the amine becomes non-integral, approaching two in the presence of an excess of the amino-component. Probably the second amine molecule enters into the transition state and evidently functions, instead of alcohol, as a proton transfer agent[256]. The rate of addition of t-butylamine to *meta*- and *para*-substituted aryl vinyl sulphones $RC_6H_4SO_2CH{=}CH_2$ (R = H, CH_3, CH_3O, Cl, NO_2, or CH_3SO_2) is satisfactorily correlated with the Hammett relation ($\rho = 1.59$)[257]. This also suggests that the reactions take place via a co-ordinated mechanism with very marked charge separation and a high degree of new bond formation in the transition state. According to kinetic data[259], the introduction of a methyl group in the β-position in the double bond of the *p*-tolyl vinyl sulphone molecule lowers the rate of addition of piperidine by a factor of 840 and in the case of α-substitution the rate falls by a factor as high as 6500. The explanation given for this behaviour is similar to that

discussed above for substituted acrylonitriles—destabilisation of the carbanionic centre in the transition state as a result of the donor properties of the methyl group[259].

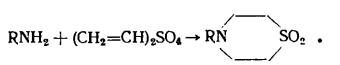
There are data (mainly in patents) on the addition of aromatic amines, but these probably require experimental verification: thus *N*-ethylaniline can add to *p*-tolyl vinyl sulphone on heating to 100°C[253], β-naphthylamine reacts satisfactorily on being refluxed in methanol, and *o*-aminobenzenesulphonic acid and amines of similar structure react in aqueous sodium carbonate solutions[252,253]. Data have also been published on the acceleration of the reaction in the presence of benzoyl peroxide or zinc acetate[253]. Weakly basic aromatic amines such as *p*-nitroaniline and diphenylamine apparently react only in the presence of alkaline additives (metallic potassium, sodium hydroxide)[253,254].

Divinyl sulphone, which can interact with secondary amines in proportions of 1:1 and 1:2, exhibits high chemical reactivity[260-263]. Most of the bis-addition reactions take place with high yields in the presence of an excess of the amino-component even at room temperature or with slight heating[260,262]. For this reason, the formation of monoadducts is favoured by dilution of the reactant mixture with a non-polar solvent and by cooling (for example in ether at a temperature between −1° and −3°C)[263]. The condensation of divinyl sulphone and pyridine hydrochloride and some of its substituted derivatives has been described[260,264]:



The reaction is reversible and takes place rapidly only in an almost neutral alcoholic medium (pH 6.5–7.5). An increase of acidity, which leads to binding of part of the tertiary amine, sharply inhibits addition processes.

On heating with divinyl sulphone, primary amines cyclise in most cases to 1,1-dihydroxy-1,4-thiazane derivatives[256,266]:



Diamines, aniline, hydroxylamine, phenylhydrazine, and amino-acids and their esters react by the same mechanism. The reactions are accelerated in the presence of alcohol. Somewhat longer heating and a somewhat greater amount of solvent are required for higher and especially aromatic amines[266].

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Karpov Moscow Physicochemical Institute
Department of Organic Chemistry,
Moscow State University

U.D.C. 541.128:537.311

Advances in the Synthesis of α-Ethynylcarbonyl Compounds

R.I.Katkevich and L.I.Vereshchagin

The methods of synthesis of α-ethynylcarbonyl compounds are discussed. Attention has been concentrated on the methods of synthesis of preparative value. Despite the practical approach employed, the review deals with a large number of studies devoted to methods of purely theoretical interest. The biliography includes 215 references.

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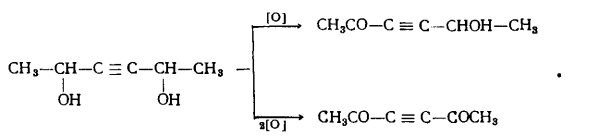
I. INTRODUCTION

In recent years there has been a considerable growth of interest in the chemistry of ethynylcarbonyl compounds for two reasons. Firstly, ethynyl ketones contain several reaction centres in the molecule and therefore can be legitimately included amongst synthetically promising substances, and, secondly, many ethynyl ketones isolated from plant raw material have shown antibiotic properties. This is particularly important because, despite the application of wide-spectrum antibiotics discovered recently, there is an urgent need in clinical chemotherapy for new antibacterial preparations and continuous and intensive research in this field is necessary. The chemistry of acetylene has been developing very rapidly. Whereas acetylene itself, ethynyl alcohols, and acetylenic acids have been extensively reviewed, no reviews are as yet available on the methods of synthesis and the chemistry of ethynylcarbonyl compounds. In this sense the present review is essentially the first attempt to set out the principal information available on this problem. The data on which the review is based were selected from the standpoint of their practical value. Attention has been concentrated on the methods of synthesis of α-ethynylcarbonyl compounds which, in the authors' view, are the most interesting representatives of this class of compounds, and also on the assessment of these methods and the elucidation of the limits of their applicability. It should, however, be noted that the generally known and widely used methods of preparation of aliphatic ketones and aldehydes in most cases cannot unfortunately be extended to ethynyl compounds. On the other hand, among synthetic methods for the latter, many are exceptionally specific and there is no prospect of their general employment.

II. OXIDATION OF ETHYNYL ALCOHOLS AND HYDROCARBONS

One of the most widely used synthetic methods for ethynylcarbonyl compounds is the oxidation of the corresponding primary and secondary carbinols and certain hydrocarbons. A wide variety of oxidising agents may be used for the oxidation of alcohols, but the presence in the ethynylcarbinol molecule of a group as reactive as the triple bond narrows considerably the range of acceptable oxidants. The application of vigorous oxidising agents such as, for example, potassium permanganate or nitric acid is undesirable because of the consequent disruption of the multiple bond by the agent.

Historically, the first oxidising agent employed was chromium trioxide CrO_3. Andre[1] was the first to employ chromium trioxide in acetic acid solution for the preparation of ethynyl ketones. Depending on the reactivity and the stability of the alcohol, this oxidising agent can be used in combination with various solvents at different temperatures. The nature of the solvent employed, the concentration of the reactants, and temperature have an appreciable effect on the reaction. Thus various aliphatic, aromatic, and heterocyclic ethynyl ketones have been obtained by the action of chromium trioxide in sulphuric acid[2-6]. Secondary diethynyl carbinols[7-12], vinylethynyl carbinols[6,13], acetylenic hydroxy-acids[14,15], and ethynyl glycols[2,16-18] are oxidised under similar conditions. It was noted that aliphatic glycols are oxidised with much greater difficulty than aromatic glycols[2]. Compared with diaroylacetylenes, the yields of the analogous aliphatic diketones are much lower, which is probably due to their low stability. Primary and secondary hydroxy-groups are oxidised. By selecting the reaction conditions and the starting material: : oxidant ratio, it is possible to achieve the oxidation of only one of the hydroxy-groups[2,19]:



Thus in the oxidation of hex-3-yne-2,5-diol by an equimolar amount of chromium trioxide in sulphuric acid at low temperatures the product was 2-hydroxyhex-3-yn-5-one. Using an excess of chromium trioxide, it is possible to convert the glycol into the corresponding diketone. To oxidise more unstable alcohols and glycols, less reactive solutions of chromium trioxide in acetone[20-22] or in acetic acid[23-26] are employed. Recently a chromium trioxide–pyridine complex was proposed for the oxidation of ethynyl

carbinols[27-29]. Owing to the mildness of the reaction conditions, the method gives good results; the replacement of pyridine by acetone as the solvent impairs the yields.

Very contradictory data have been published on the oxidation of primary ethynyl alcohol. Thus Jones and coworkers[30,31] showed that the oxidation of primary alcohols and glycols with chromium trioxide in acetone does not stop at the stage involving the formation of the carbonyl compound. The reaction takes place with formation of mono- and di-carboxylic acids, the yields of which vary from 20 to 40%.

At the same time Wille et al.[32], who oxidised propargyl alcohol by the same oxidising agent, and also Jacobs et al.[33], who oxidised 1-phenylpent-3-en-1-yn-5-ol, obtained the corresponding aldehydes in a yield of about 50%. These different results are associated with the different duration of contact between the reactants and their relative amounts.

The problem of the mechanism of the oxidation of various alcohols by chromium trioxide has been widely discussed. Two principal hypotheses concerning the oxidation mechanism have been put forward on the basis of numerous kinetic studies: Westheimer's so called "ether" mechanism[34] and the mechanism in which the dissociation of hydrogen as the hydride ion is postulated[35]. The above data clearly show the large scale of the application of chromium trioxide for synthetic purposes. However, a certain limitation of this method should also be noted: many highly unsaturated ketones, which are very sensitive to the acidity of the medium, cannot be obtained by this method. Potassium dichromate is less often used for the oxidation of alcohols[36].

In recent years new oxidising agents with a wide range of activity and high selectivity have been found. Among these, activated manganese dioxide obtained in 1948 and extensively used for the oxidation of a wide variety of different classes of compounds occupies a prominent place. Monoethynyl[37-39], vinylethynyl, and polyethynyl ketones[40-42], and ethynyl, vinylethynyl, and polyethynyl aldehydes[43-45] have been synthesised with the aid of activated manganese dioxide. Glycols[17,46] and esters of acetylenic hydroxy-acids[28] are oxidised less successfully. A characteristic feature of this reaction is the lack of sensitivity of the carbon framework, in particular the double and triple bonds, to the action of the oxidant. Because of the specificity of its action, activated manganese dioxide is justifiably regarded as the most convenient and almost irreplaceable dehydrogenating agent for the oxidation of highly unsaturated and extremely unstable hydroxy-compounds. The oxidation is carried out under a wide variety of conditions: with various solvents, in a fairly wide range of temperatures, and with different proportions of the components. It has been established empirically[47,48] that the polarity of the solvent has a very significant effect on the rate and mode of this reaction.

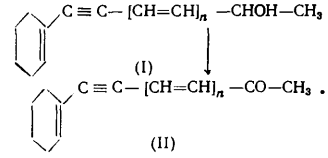
It is considered more desirable to employ chloroform, benzene, pentane, and ether than acetone, since the degree of deactivation of activated manganese dioxide is directly related to the polarity of the solvent employed. The most highly deactivating solvents are aliphatic alcohols, particularly tertiary alcohols; acetone and ethyl acetate also deactivate the oxidant, but much less. The duration and temperature of the reaction depend on the activity of the manganese dioxide, the substance to be oxidised, and the proportions of the components. To reduce its duration, the reaction is frequently carried out at an elevated temperature. The test substance : reactant weight ratio is usually varied in the range 1 : 5–1 : 20 and in some cases 1 : 50. According to many investigators, the ease of oxidation depends on the adsorbability of the given compound on the oxidant. Experimental confirmation has been obtained[40] for the earlier hypothesis of Ball et al.[50] that the more saturated compounds, which are less well adsorbed on the oxidant, should react at a lower rate. However, the degree of adsorption is scarcely the sole factor determining the rate of reaction.

Pratt proposed a free-radical mechanism for the oxidation by activated manganese dioxide[51,52]:

$$R_2CHOH + O{=}Mn{=}O \rightarrow R_2\dot{C}OH + HO{-}Mn{=}O \rightarrow$$
$$\rightarrow R_2\dot{C}{-}\dot{O} + HO{-}Mn{-}OH \rightarrow R_2CO + MnO + H_2O\,.$$

It must be particularly emphasised that the capacity for the selective oxidation of a hydroxyl activated by multiple bonds and an aromatic ring is one of the many specific features of manganese dioxide.

A less widely used synthetic method for ethynylcarbonyl compounds is based on the Oppenauer oxidation of ethynyl alcohols. On prolonged refluxing with aluminium t-butoxide in acetone–benzene solution, ehtynyl carbinols are converted into the corresponding ketones[53-56]:



(I) (II)

It has been noted that the ethynyl alcohols (I) with $n = 0$ react slowly with this oxidising agent. An increase in the number of double bonds has a favourable effect on the reaction and leads to an improvement of the yield of the ketones (II).

Nickel peroxide and manganese acetate are less widely used oxidising agents but give good results[57,58,59]. Nickel peroxide is more often used[57]; the reaction is carried out in a neutral medium, since in an alkaline medium primary alcohols are converted into acids. The yields of the desired products are fairly high.

A satisfactory result was obtained in the oxidation of ethynyl and vinyl alcohols by quinones[60]. Thus 1,5-diphenylpent-4-en-1-yn-3-ol mixed with *o*-chloranil in an alcoholic solution gives at room temperature the ethynyl vinyl ketone (III) in 91% yield:

$$Ph{-}C{\equiv}C{-}\underset{OH}{CH}{-}CH{=}CH{-}Ph \rightarrow Ph{-}C{\equiv}C{-}CO{-}CH{=}CH{-}Ph\,.$$
(III)

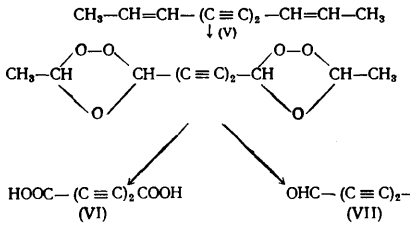
Together with the oxidation of the alcoholic group, ketones are also prepared by a method involving the dissociation of unsaturated compounds at the double bond. The double bond in vinylethynyl compounds is known to be oxidised by peracids much faster than the triple bond and the rate of oxidation increases with the number of substituents at the double bond. This feature was used to synthesise ethynyl ketones[61]. Acetylacetylene and vinylacetylacetylene have been synthesised by heating isopropenylacetylene and isopropenylvinylacetylene with hydrogen peroxide for 35–40 h at 35–45 °C in acetic acid and acetic anhydride. Sometimes monoacetates derived from the alcohols (IV) are formed together with the ketones:

$$R{-}C{\equiv}C{-}\overset{CH_3}{\underset{|}{C}}{=}CH_2 \xrightarrow{CH_3COOH} R{-}C{\equiv}C{-}CO{-}CH_3 + R{-}C{\equiv}C{-}\overset{OOCCH_3}{\underset{|}{C}}{-}CH_3\,,$$
(IV)

where R = H or $CH{=}CH_2$.

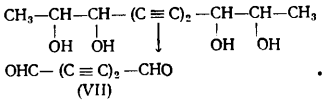
The double bond in enynes is also more sensitive than the triple bond to the action of ozone. This difference in the reactivities of the multiple bonds has been used for

preparative purposes [62]. It has been established that the reaction of dienediynes (V) with ozone takes place smoothly with formation of diozonides, the acid hydrolysis of which gives the acetylenic acids (VI) in 65% yield. At the same time the reductive dissociation of ozonides with zinc dust in water or dioxan makes it possible to obtain a good yield even of the highly unstable diethynyl dialdehyde (VII)

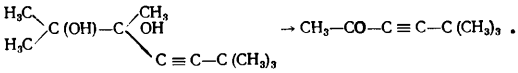


However, this method is more suitable for the synthesis of acetylenic acids than aldehydes.

One of the methods for the synthesis of aliphatic carbonyl compounds is the cleavage of the carbon chain of α-glycols between the hydroxylated carbon atoms with lead tetra-acetate, sodium periodate, and periodic acid. This method has also been successfully used in the acetylenic series. Bohlmann and coworkers employed sodium periodate and periodic acid for the dissociation of diols. Thienylpropiolic aldehyde [63], α-hexynal [64], and the diethynyl dialdehyde (VII) were obtained in this way [62]:

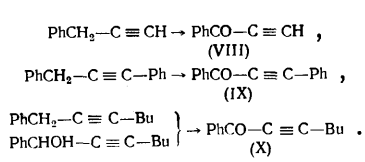


The oxidation of α-glycols with lead tetra-acetate also takes place relatively easily [65]. It is sufficient to heat the diol for 2–3 h to 60–65°C in glacial acetic acid with a 20% excess of the oxidising agent [66,67]:

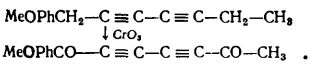


Depending on the structure of the initial glycol, it is possible to obtain by this method both aldehydes and ketones [68]. The method cannot be regarded as preparative, but it is very convenient for the identication and the demonstration of the structures of organic substances.

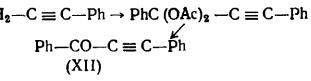
Iwai and Okajima [69-71] introduced the carbonyl group into acetylenic compounds by direct oxidation of the propargylmethylene group with selenium dioxide. Ethynyl ketones (VIII), (IX), and (X) were obtained by prolonged refluxing of the hydrocarbon with sublimed selenium dioxide in alcohol or in a 1 : 1 alcohol–dioxan mixture.



The reaction takes place more unambiguously and a smaller number of side products are formed when the propargylmethylene group is activated by other multiple bonds. By selecting the experimental conditions, the reaction can be stopped at the stage involving the formation of the carbinol [69,70]. On the other hand, there are indications in the literature that primary and secondary ethynyl alcohols can be oxidised to the corresponding ketones and aldehydes [71,72]. The yields of the required products vary in the range 5–27%. Despite its apparent simplicity, the method has not found wide application because of the toxicity of selenium dioxide and the difficulty of obtaining the initial acetylenic hydrocarbons. Together with selenium dioxide, chromium trioxide in acetic acid [73] and lead tetra-acetate [74] have been used to oxidise the propargylmethylene group:

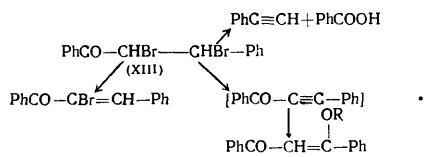


Benzylethynyl hydrocarbons exchange the hydrogen atom activated by the adjacent triple bond and the phenyl ring for the acetoxy-group on treatment with lead tetra-acetate. Thus the interaction of triphenylpropyne with lead tetra-acetate in acetic acid at 100°C gave the diacetate (XI), which was hydrolysed to diphenylpropynone (XII) by refluxing with a solution of sodium carbonate:

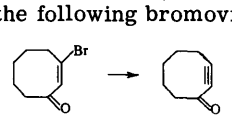


III. THE DEHYDROHALOGENATION REACTION

The most widely employed method of synthesis of ethynyl compounds is dehydrohalogenation of halogeno-derivatives. However, in the series of ethynylcarbonyl compounds the application of this method is very limited because of the exceptional reactivity of the α-ethynylcarbonyl group. The triple bond of α-ethynyl ketones is highly activated by the adjacent carbonyl group and readily undergoes various nucleophilic addition reactions [75,76]. The dehydrohalogenation of dihalogeno-derivatives is performed using alcoholic solutions of alkalis or sodamide in liquid ammonia. These methods, with few exceptions, are unsuitable for the synthesis of ethynyl ketones. In 1904 Watson [77] attempted to prepare phenylbenzoylacetylene from dibromobenzylideneacetophenone and α-bromobenzylideneacetophenone. He found that, when the halogeno-ketone (XIII) is treated with alcoholic alkali, the reaction takes place in different ways depending on the conditions:



Under mild conditions, the reaction does not go to completion. Only one molecule of hydrogen bromide is dissociated from dibromobenzylideneacetophenone. After prolonged refluxing, the alcohol addition product, β-ethoxybenzylideneacetophenone, was isolated. The reaction does not occur in water and, when attempts are made to split off hydrogen bromide with solid alkali, the molecule is cleaved into phenylacetylene and benzoic acid [78]. Under the action of potassium carbonate, it was possible to dehydrobrominate the following bromovinyl ketones [79]:



Dehydrohalogenation with pyridine and sodium acetate stops at the stage involving the formation of the monohalogeno-derivative [80]. When the monobromo-ketones are treated with ammonia and primary or secondary amines,

the halogen is usually substituted by an amino-group. On the other hand, after dehydrochlorination of the β-chlorovinyl ketone (XIV) with sodamide in liquid ammonia, the ethynyl ketone (XV) was isolated[81]:

$$\underset{\text{(XIV)}}{\text{R—CO—CH=CHCl}} \rightarrow \underset{\text{(XV)}}{\text{R—CO—C}\equiv\text{CH}} .$$

R= ferrocenyl

Reactions involving addition to the triple bond can be avoided in certain cases when the dehydrohalogenation is carried out with a base in solvents such as benzene or acetone[78,82]. The use of triethylamine in benzene or in acetone permits the synthesis of dibenzoylacetylene from the dibromide (XVI)[82] in 82–95% yield and also from the monochloride (XVII)[83]:

$$\left.\begin{array}{l}\text{ArCO—CHBr—CHBr—CO—Ar}\\ \text{(XVI)}\\ \text{Ar—CO—CCl=CH—CO—Ar}\\ \text{(XVII)}\end{array}\right\} \rightarrow \text{ArCO—C}\equiv\text{C—CO—Ar} .$$

It is noteworthy that Japanese chemists[84] succeeded in obtaining ethynyl phenyl ketone in the usual way by the dehydrochlorination of the dichloro-derivative with alcoholic alkali, the mixture being refluxed for 5 h. However, these results are somewhat doubtful.

Compounds with a protected carbonyl group are more successfully dehydrohalogenated. Claisen obtained the first ethynyl aldehyde as early as 1896 by the dehydrobromination of the dimethylacetal of dibromopropionaldehyde[85]:

$$\text{R—CHBr—CHBr—CH(OR')}_2 \xrightarrow[\text{ROH}]{\text{KOH}} \text{R—C}\equiv\text{C—CH(OR')}_2 \xrightarrow{\text{H}_3^+\text{O}} \text{R—C}\equiv\text{C—CHO} .$$

Subsequently this method became one of the principal procedures for the synthesis of α-ethynyl aldehydes[86–90]. The protective acetal group prevents side reactions and its removal by hydrolysis in an acid medium does not involve any special complications[91].

IV. INTERACTION OF METAL ACETYLIDES AND IOTSICH REAGENTS WITH ACID DERIVATIVES

1. Reaction of Metal Acetylides and Iotsich Reagents with Acid Halides

Until the 1940's ethynyl ketones were obtained mainly by the condensation of alkali metal acetylides and acid halides. Thus in 1899 Nef[92] was the first to obtain phenylacetylacetylene and phenylbenzoylacetylene by the action of sodium phenylacetylide in ether on acetyl and benzoyl chlorides respectively:

$$\text{R—COCl} + \text{NaC}\equiv\text{C—Ph} \rightarrow \text{R—CO—C}\equiv\text{C—Ph} ,$$

where R = methyl or phenyl.

Later this reaction was extended to other acetylenic hydrocarbons and acid halides[93–96]. Sodium, potassium, and lithium acetylides were employed. Sodium phenylacetylide proved to be convenient for preparative purposes. In some cases acid bromides react under milder conditions than the corresponding acid chlorides[2,96,97]. It has been shown[93] that the reaction of sodium phenylacetylide with benzoyl chloride is complicated by side reactions. The ethynyl ketone formed reacts readily with a second molecule of acetylide, yielding the corresponding tertiary carbinol. For this reason, the method gives unsatisfactory yields of the desired products, which are contaminated by carbinols and halogeno-compounds. Good results were achieved only in the synthesis of relatively unreactive nitroarylethynyl ketones and similar compounds[98,99]:

$$\text{m-NO}_2\text{C}_6\text{H}_4\text{COCl} + \text{NaC}\equiv\text{C—Ph} \rightarrow \text{m-NO}_2\text{C}_6\text{H}_4\text{CO—C}\equiv\text{C—Ph} ,$$

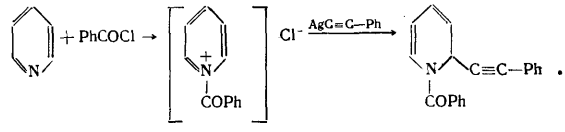
$$\text{m-NO}_2\text{C}_6\text{H}_4\text{C}\equiv\text{C—COCl} + \text{NaC}\equiv\text{C—Ph} \rightarrow \text{m-NO}_2\text{C}_6\text{H}_4\text{C}\equiv\text{C—CO—C}\equiv\text{C—Ph} .$$

The attempt to prepare the symmetrical ketone from sodium ethylacetylide and phenylpropiolic acid chloride was unsuccessful[100]. However, Chauvelier[24], who carried out this reaction with care, succeeded in synthesising 1,5-diphenylpenta-1,4-diyn-3-one, which was characterised as the hydrazone. In 1936 Kroeger and Nieuwland showed that the substitution of metal acetylides by the Iotsich reagent gives more satisfactory results[101]. It is best to employ ethynylmagnesium chloride derivatives; these are less reactive than the analogous bromides and iodides, which readily take part in secondary reactions[102–104]. The use of silver acetylides, which do not interact with the carbonyl group, excludes the possibility of the appearance of side products. By heating silver phenylacetylide with benzoyl chloride, Nef[92] obtained 1,3-diphenylprop-1-yn-3-one in a high yield. It is more convenient to carry out this reaction with silver derivatives soluble in carbon tetrachloride, chloroform, or benzene. In some cases the normal course of the reaction requires the addition of aluminium chloride[105]. The same paper describes the synthesis of halogenoethynyl ketones from silver acetylides and halogeno-carboxylic acid chlorides:

$$\text{X—CH}_2\text{COCl} + \text{AgC}\equiv\text{C—R} \rightarrow \text{X—CH}_2\text{CO—C}\equiv\text{C—R},$$

where X = Cl or Br and R = C_4H_9 or C_6H_{13}.

The synthesis of these ketones from sodium acetylides results in very low yields. Silver acetylides are much more soluble in pyridine[106] but the reaction in this solvent mainly gives rise to the formation of *N*-acyl-2-alkynyl-2-dihydropyridine:



The possibility of preparing α-ethynyl ketones by the reaction of copper acetylides with acid halides is of some interest[107]. The authors determined the conditions under which the desired products are formed with very satisfactory yields (up to 45%):

$$\text{PhCOCl} + \text{CuC}\equiv\text{C—Ph} \rightarrow \text{PhCOC}\equiv\text{C—Ph} .$$

Organozinc and organocadmium compounds, which have found wide application in the synthesis of saturated and vinyl ketones, are more promising in this type of process. The attempts to extend this method to ethynyl ketones proved to be unsuccessful[108] and only in recent years has it been established[109] that phenyl- and vinyl-acetylenes form ethynylzinc iodides by the reaction with solutions of alkylzinc iodides. The reaction of ethynylzinc iodides with aliphatic and aromatic acid chlorides gives rise to the corresponding ethynyl ketones. The reaction involves considerable charring, which is reduced when ethynylzinc chlorides are employed. The yields of ketones reach 40–70%. Similar results were obtained with ethynylcadmium halides[110]. The ethynylcadmium halide reagent was obtained by the action of cadmium chloride on the ethylnylmagnesium halide derivative. The reagent thus formed reacts with mono- and di-carboxylic acid chlorides, giving rise to the formation of ethynyl ketones in 40–70% yield. Ethynyl ketones were obtained similarly from an ethynyllead reagent[111].

Recently Gavrilenko et al.[112] suggested that complex aluminium acetylides, which can be readily obtained from lithium, potassium, or sodium aluminium hydrides and monosubstituted acetylenes in tetrahydrofuran, diglyme [2-methoxyethyl ether (Ed. of Translation)], or pyridine, be used for the synthesis of ethynyl ketones:

$$MAlH_4 + RC{\equiv}CH \rightarrow MAl(C{\equiv}C{-}R)_4 + 4H_2 \ .$$
(XVIII)

Under certain conditions, the complex acetylides (XVIII) are formed strictly selectively without the addition of lithium aluminium hydride to the triple bond. The interaction of complex aluminium acetylides with acid chlorides is carried out at 29–40°C and with acid anhydrides at 70°C:

$$MAl(C{\equiv}C{-}R)_4 \xrightarrow{R'COCl} R'CO{-}C{\equiv}C{-}R$$
$$MAl(C{\equiv}C{-}R)_4 \xrightarrow{(R''CO)_2O} R''CO{-}C{\equiv}C{-}R \ .$$

When the temperature is raised in excess of the above limits, charring becomes more extensive and the yields of ethynyl ketones, which even under optimum conditions are only 20–40%, are reduced. Thus this method is hardly likely to find wide application.

2. Interaction of Alkali Metal Acetylides and Iotsich Reagents with Acid Anhydrides

Although as early as 1899, Nef[92] indicated the possibility in principle of synthesising ethynyl ketones from sodium acetylides and acetic anhydride, it was not until 1936 that Kroeger and Nieuwland[101] made a detailed study of this reaction and demonstrated the advantage of anhydrides over acid chlorides. It was established that much better results are achieved, as with acid chlorides, when Iotsich reagents are employed instead of alkali metal acetylides. The relatively unreactive ethynylmagnesium chlorides are preferable to the bromides and iodides, which largely favour the occurrence of side reactions involving the formation of ethynyl carbinols:

$$(CH_3CO)_2O + R{-}C{\equiv}C{-}MgCl \rightarrow R{-}C{\equiv}C{-}CO{-}CH_3 \ .$$

The yields of ethynyl ketones in this reaction are in the range 40–80%. According to Nieuwland, more satisfactory results are obtained in reactions with alkylacetylenes when the anhydride is added to the Iotsich reagent at −25°C. When condensations of this kind are carried out in the range between −50° and −70°C, the yields of the desired products are improved[113–115]. When the reaction is carried out at room temperature, the reagents must be mixed in the reverse order (i.e. ethynylmagnesium halide must be added carefully to the anhydride) to prevent more completely the occurrence of side effects. This method was used successfully in the synthesis of ethynyl ketones with aliphatic substituents[113,114,116–118] and cycloalkyl-[119,120], silylethynyl-[115,121], and asymmetric vinylethynyl-carbonyl compounds[122].

The reaction of sodium acetylides with acid anhydrides yields the corresponding ketones, but there are many exceptions[123]. Symmetrical vinylethynyl ketones (XIX) were obtained in satisfactory yields from the anhydrides of cinnamic, crotonic, succinic, and maleic acids and sodium phenylacetylide[108,109]:

$$\begin{matrix} PhCH{=}CH{-}CO \\ \qquad\quad O + NaC{\equiv}C{-}Ph \rightarrow PhCH{=}CH{-}CO{-}C{\equiv}C{-}Ph \ . \\ PhCH{=}CH{-}CO \end{matrix}$$
(XIX)

The attempt to obtain the analogous ketones from the anhydride of acrylic acid and ethynylmagnesium chlorides or lithium acetylides was unsuccessful[124]. Either the starting materials were recovered unchanged or the yield of reaction products was unsatisfactory.

The use of lithium acetylides as the acetylenic component leads to the formation of tertiary ethynyl carbinols. The preferential formation of alcohols can be explained by the high solubility of the lithium complex in ether and its capacity for the ready formation of the ketone, the subsequent reaction of which with a second molecule of the acetylide no less readily gives rise to the ethynyl alcohol, which is undesirable in this case. However, in many studies it was noted that, when the condensation of lithium acetylides with acid anhydrides is carried out at temperatures of the order of −80°C, it is possible to stop the process at the stage where the carbonyl compound is formed[125]. The interaction of lithium acetylides with cyclic anhydrides of dicarboxylic aliphatic[126], alicyclic, and aromatic acids[127] leads to the formation of α-ethynyl keto-acids in high yields. The attempts to employ in this synthesis ethynylmagnesium bromides and the analogous ethynylmagnesium chlorides were unsuccessful.

In order to suppress the side reaction involving the formation of acetylenic hydroxy-acids, the condensation must be carried out at a temperature between −5° and 30°C.

3. Interaction of Nitriles, Amides, and Salts with Iotsich Reagents and Alkali Metal Acetylides

The method of preparation of saturated ketones from Grignard reagents and saturated nitriles is generally known. Ethynylmagnesium derivatives are much more reactive than the saturated and aromatic derivatives. However, even these yield the corresponding ethynyl ketones on reaction with aliphatic and aromatic acid nitriles and amides. Thus diphenylpropynone was obtained by the reaction of phenylethynylmagnesium bromide with benzonitrile[128]. On the other hand, Iotsich reagents do not react either with acetonitrile or acetamide[101]. The nitriles of substituted propiolic acid react fairly less readily with ethynylmagnesium compounds, giving high yields of diethynyl ketones[129]:

$$R{-}C{\equiv}C{-}CN + R'{-}C{\equiv}C{-}MgBr \rightarrow RC{\equiv}CC(=NMgBr)C{\equiv}CR' \xrightarrow{H_2O} RC{\equiv}CCOC{\equiv}CR' \ .$$

In a study of the reaction between a Grignard reagent and the nitrile of β-bromocrotonic acid, Boularand and coworkers showed that the reaction involves an elimination–addition mechanism[130]:

$$CH_3CBr{=}CH{-}CN \xrightarrow{RMgX} CH_3{-}C{\equiv}C{-}CN \xrightarrow{RMgX}$$
$$CH_3{-}C(R){=}CHCN + CH_3{-}C{\equiv}C{-}CO{-}R \ ,$$

where R = methyl or ethyl.

The use of aromatic organomagnesium compounds makes it possible to obtain as the sole reaction product arylated nitriles of the type $CH_3{-}C(Ar){=}CH{-}CN$. The reaction of β-mesityl-β-methoxyacrylonitrile with phenylmagnesium bromide involves a 1,2-addition mechanism with formation of benzoylmesitylacetylene[131].

In 1903 a method was proposed for the synthesis of saturated aldehydes from disubstituted formamides and Grignard reagents [132]. Later this method found fairly wide application for the syntheses of aldehydes of the ethynyl [63,133] and vinylethynyl series [134]:

$$R{-}C{\equiv}CMgBr + (CH_3)_2NCHO \rightarrow R{-}C{\equiv}C{-}CH\,N(CH_3)_2OMgBr \xrightarrow{H_2O+} R{-}C{\equiv}C{-}CHO\,.$$

The reaction of acetamides with ethynylmagnesium bromides yields the corresponding ethynyl ketones [135]. Anomalies were observed in this reaction. For example, Viguer [136], in his attempt to obtain tetrolic aldehyde from diethylformamide and propynylmagnesium bromide, obtained 4-diethylaminohepta-2,5-diyne by the reaction:

$$HCON(C_2H_5)_2 + CH_3C{\equiv}CMgBr \rightarrow CH_3C{\equiv}C{-}\underset{\displaystyle OMgBr}{\underset{|}{CH}}{-}N(C_2H_5)_2 \xrightarrow{CH_3C{\equiv}CMgBr} \rightarrow CH_3C{\equiv}C{-}\underset{\displaystyle N(C_2H_5)_2}{\underset{|}{CH}}{-}C{\equiv}C{-}CH_3\,.$$

As in the case where the Iotsich reagent is employed, the reaction of heptynyl-lithium bromide with acetamide does not yield ethynyl ketones, the acetylenic hydrocarbon being regenerated [101].

Vinylamino-ketones (XX) and vinylamino-aldehydes (XXI), which are vinylogues of carboxylic acid amides, react with Iotsich reagents via the following mechanism:

$$R{-}C{\equiv}CMgBr + \underset{R'}{\overset{R'}{>}}N{-}CH{=}CH{-}CO{-}R'' \rightarrow R{-}C{\equiv}C{-}CH{=}CH{-}CO{-}R'',$$

(XX)

$$R{-}C{\equiv}C{-}MgBr + \underset{Me}{\overset{Ph}{>}}N{-}CH{=}CH{-}CHO \rightarrow R{-}C{\equiv}C{-}CH{=}CH{-}CHO\,,$$

(XXI)

yielding vinylethynylcarbonyl compounds [137,138].

Salkind [139] established that aldehydes and ketones may be prepared by the reaction between Grignard reagents and anhydrous salts of formic and acetic acids. Later this reaction was used to synthesise ethynylcarbonyl compounds. Thus in the reaction with methylmagnesium iodide sodium phenylpropiolate is converted into phenylacetylacetylene [140]. A similar result was obtained in the reaction of an excess of methyl-lithium with free propiolic acid [141]. Phenylmagnesium bromide and phenyl-lithium do not enter into this reaction. In this case the yields of ketones are usually lower than when acid chlorides, amides, and nitriles are employed and therefore the reaction has not been used for preparative purposes.

4. Interaction of Iotsich Reagents and Ethynyl Derivatives of Alkali Metals with Esters

Usually the reaction of formic acid esters with Grignard reagents yields secondary alcohols. However, Gattermann [142], who used an excess of the ester, cooled the system intensively, and mixed the reagents in the reverse sequence, succeeded in driving the process towards the formation of aldehydes. Under similar experimental conditions, Iotsich reagents can be used successfully because of their relatively lower reactivity [143]. Formate esters react with equimolar amounts of alkali metal acetylides to form the corresponding aldehydes [144-146], but this synthesis is relatively inconvenient, since, even when the experimental conditions are rigorously maintained, ethynyl aldehydes are formed in a mixture with alcohols and the yield does not exceed 30%. Iotsich [146-149] made a fairly detailed study of the interaction between carboxylic acid esters and ethynylmagnesium derivatives:

$$CH_3COOC_2H_5 + R{-}C{\equiv}CMgBr \rightarrow R{-}C{\equiv}C{-}CO{-}CH_3 \xrightarrow{R{-}C{\equiv}CMgBr} \rightarrow (R{-}C{\equiv}C)_2C(OH){-}CH_3\,.$$

The primary reaction products are ketones. With ethyl acetate and higher carboxylic acid esters, ketones could not be isolated and therefore the sole reaction products were tertiary diethynyl alcohols [150-152]. Condensation of ethynylmagnesium compounds with ethyl benzoate also yields ethynyl carbinols [153]. Esters of acids with a triple bond, including the α-position, behave similarly. Ethyl phenylpropiolate reacts in this way with methylmagnesium iodide, phenylmagnesium bromide [140], and tolylmagnesium bromide [154]:

$$PhC{\equiv}C{-}COOC_2H_5 + 2\,CH_3MgI \rightarrow PhC{\equiv}C{-}\underset{\displaystyle OH}{\underset{|}{C}}(CH_3)_2\,.$$

On the other hand, Hurd [155], who started with ethyl phenylpropiolate and phenylmagnesium bromide, obtained 1,3-diphenylprop-1-yn-3-one in 85% yield. The interaction of ethyl cinnamate with sodium phenylacetylide gives rise to the ethynyl vinyl ketone (XXII) [156]:

$$PhCH{=}CH{-}COOC_2H_5 + PhC{\equiv}CNa \rightarrow \underset{(XXII)}{PhCH{=}CH{-}CO{-}C{\equiv}C{-}Ph}\,.$$

However, the formation of compound (XXII) has been inadequately demonstrated, since the analogous ketone obtained from cinnamic acid anhydride and sodium phenylacetylide differs sharply from it in its physical constants and chemical properties [109]. The reaction of oxalic esters with Iotsich reagents has been successfully used to synthesise the esters of ethynyl keto-acids [157]:

$$R{-}C{\equiv}C{-}MgBr + C_2H_5OOC{-}COOC_2H_5 \rightarrow R{-}C{\equiv}C{-}CO{-}COOC_2H_5\,.$$

The method of synthesis is simple and convenient, consisting in mixing the ethereal solutions of equimolar amounts of alkyl- or aryl-ethynylmagnesium bromides and oxalic acid esters at a temperature not exceeding 5°C. When the alkoxy-group in the ester becomes more complex, the yield of reaction products increases.

5. Synthesis of Ethynyl Ketals and Acetals and Their Hydrolysis to Ethynyl Ketones and Aldehydes

Chichibabin [158] and Bodroux [159] showed that the orthoformic ester reacts with organomagnesium derivatives to form acetals. This reaction is one of the best procedures for the preparation of aldehydes by the Grignard reaction and is superior as regards yields and the availability of the reactants to other methods of synthesis of aldehydes (from carboxylic acid esters, formic acid salts, amides, etc.). The orthoformic acid ester reacts smoothly with an equimolar amount of the Iotsich reagent, forming ethynyl acetals in yields of 75–80%: [143,160-162]

$$R{-}C{\equiv}CMgBr + HC(OR')_3 \rightarrow R{-}C{\equiv}C{-}CH(OR')_2 \xrightarrow{H_2O^+} R{-}C{\equiv}C{-}CHO\,.$$

In the decomposition of the organomagnesium complex either the acetal or the ethynyl aldehyde directly can be isolated, depending on the conditions. The reaction of

ethynylenedimagnesium dibromide with orthoformate constitutes a simple and convenient synthesis of the diacetal of butynedial[163]:

$$BrMgC{\equiv}C{-}MgBr + HC(OR)_3 \rightarrow \underset{(XXIII)}{(RO)_2HC{-}C{\equiv}C{-}CH(OR)_2} \xrightarrow{H^+} \underset{(XXIV)}{OHC{-}C{\equiv}C{-}CHO}.$$

Satisfactory results were obtained when the reaction was carried out in benzene. In ether the diacetal (XXIII) could be obtained only after refluxing for several days. The isolation of the acetylene–dialdehyde (XXIV) is difficult because of its low stability. Acetals of vinylethynyl aldehydes were synthesised by the same method[164]:

$$R{-}CH{=}CH{-}C{\equiv}CMgBr + HC(OR')_3 \rightarrow \underset{(XXV)}{R{-}CH{=}CH{-}C{\equiv}C{-}CH(OR')_2} \xrightarrow{H_2^+O} \rightarrow R{-}CH{=}CH{-}C{\equiv}C{-}CHO,$$

where R = H or alkyl.

In the hydrolysis of the acetals of vinylethynyl aldehydes (XXV) with 3% hydrochloric acid extensive charring is observed. Gusev and Kucherov showed[165,166] that the optimum conditions for the hydrolysis of the acetal (XXVI) of diacetylene-aldehyde are achieved by brief refluxing of compound (XXVI) with dilute hydrochloric acid in dioxan. The extreme lability of the aldehyde (XXVII) precludes its isolation in a pure form:

$$\begin{aligned} &H_3C\diagdown\ \ C(OH){-}C{\equiv}C{-}C{\equiv}CH + HC(OR_3) \rightarrow \ H_3C\diagdown\ \ C{-}C{\equiv}C{-}CH(OR)_2 \rightarrow \\ &H_3C\diagup\ H_3C\diagup OH \\ &\xrightarrow{KOH} \underset{(XXVI)}{HC{\equiv}C{-}C{\equiv}C{-}CH(OR)_2} \xrightarrow{H^+} \underset{(XXVII)}{HC{\equiv}C{-}C{\equiv}C{-}CHO}. \end{aligned}$$

When lithium or sodium phenylacetylide was allowed to react with the acetal of α-bromoacetaldehyde, the acetal of 4-phenylbut-3-ynal was obtained[167]:

$$PhC{\equiv}CLi + BrCH_2CH(OR)_2 \rightarrow PhC{\equiv}C{-}CH_2CH(OR)_2 \xrightarrow{H^+} PhC{\equiv}C{-}CH_2CHO.$$

Howk[168] proposed a single-stage catalytic synthesis of acetals and ketals from readily available starting materials—monosubstituted acetylenes and orthoformic esters:

$$R{-}C{\equiv}CH + HC(OR')_3 \xrightarrow{ZnX_2} R{-}C{\equiv}C{-}CH(OR')_2.$$

The suggested mechanism is as follows:

$$HC(OR)_3 + ZnX_2 \rightarrow [HC^+(OR)_2] + [ZnX_2OR^-]$$

$$HC{\equiv}CR'$$

$$\left[RO\diagdown\ \ C\diagup\ \ \overset{+}{C}H{\equiv}CR'\ \ \ H\ \ OR\right] + ZnX_2OR^- \rightarrow R'{-}C{\equiv}C{-}CH(OR)_2 + ZnX_2 + ROH.$$

The best catalysts proved to be zinc chloride, iodide, and nitrate, and also cadmium iodide. Orthoformate, orthoacetate, and orthovalerate were used as the ester components. The method of synthesis is simple, the yields of acetals and ketals varying in the range 15–80%.[169]

The acetal of tetrolic aldehyde can be obtained by treating diacetylene with ethanol and potassium hydroxide under the conditions of Favorskii's reaction[170]. When the reaction mixture is heated to 100°C, ethyl β-ethynylvinyl ether (XXVIII) is formed. The acetals are produced in appreciable amounts only at temperatures above 130°C and also when the amount of alcohol is increased. The acetal (XXIX) isomerises to the acetal of tetrolic aldehyde by the mechanism discovered by Favorskii for acetylenic hydrocarbons:

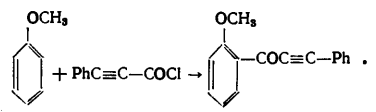
$$HC{\equiv}C{-}C{\equiv}CH{-} \begin{cases} \xrightarrow{100^\circ} \underset{(XXVIII)}{HC{\equiv}C{-}CH{=}CHOEt} \\ \xrightarrow{>130^\circ} HC{\equiv}C{-}CH_2{-}CH(OEt)_2 \xrightarrow{KOH} CH_3C{\equiv}C{-}CH(OR)_2. \end{cases}$$

(XXIX)

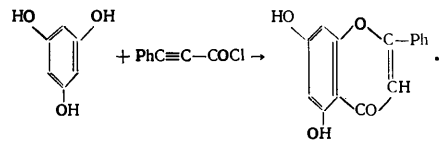
The hydrolysis of the acetals to aldehydes[91] by dilute inorganic acids causes extensive polymerisation. It has been found[171-173] that, when acetals of acetylenic aldehydes are heated with oxalic acid, it is possible to obtain aldehydes in yields of the order of 35%. Even better results are achieved when acetals are refluxed with aqueous tartaric acid with subsequent elimination using calcium chloride of the alcohol formed simultaneously. In this case the yield of tetrolic aldehyde rises to 55%.

V. ACYLATION OF AROMATIC COMPOUNDS BY ACETYLENECARBOXYLIC ACID CHLORIDES UNDER THE CONDITIONS OF THE FRIEDEL–CRAFTS REACTION

The Friedel–Crafts reaction, discovered as early as 1877, is in important method for the preparation of aromatic ketones. Its detailed and extensive study established that acylation with aliphatic carboxylic acids, their chlorides, and anhydrides is possible for a wide variety of aromatic compounds—benzene and its homologues, naphthalene and its derivatives, and also a number of heterocycles. The Friedel–Crafts reaction with the chlorides of $\alpha\beta$-unsaturated acids has been less well investigated. Experiments have shown that the acylation of aromatic compounds by the chlorides of acetylenecarboxylic acids has many limitations. The first such synthesis, carried out by Gatterman, was the acylation of anisole with the chloride of phenylpropiolic acid[174]:



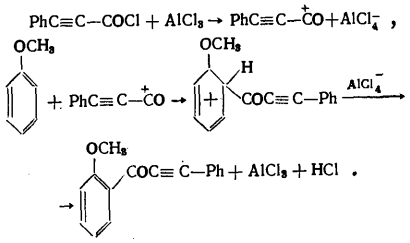
Seka and Prosche[175] also successfully employed the Friedel–Crafts condensation of phenylpropiolic acid and polyhydric phenols for the direct synthesis of hydroxyflavones:



The attempt to carry out this reaction with benzene did not result in the formation of ethynyl ketone[77]. The reported synthesis of tetradecylbenzoylacetylene under analogous conditions is doubtful[176].

The different behaviour of benzene, anisole, and phenols is probably associated with the electronic nature of the methoxy- and hydroxy-groups. If one remembers that the mechanism of this condensation includes a stage in which an acylcarbonium ion is formed with subsequent attack by the latter on the position in the benzene ring with the highest electron density then the promoting effect of HO and CH_3O groups on the acylation process becomes understandable. Other substituents with a $+I$ effect,

leading to an increase of electron density in *ortho*- and *para*-positions, should have a similar effect:



This hypothesis is confirmed by the exceptional ease of the acylation of *p*-methylanisole with the chloride of phenylpropiolic acid[177]. It is interesting that the reaction with an excess of aluminium chloride leads to the formation of chlorination products only.

The above methods of synthesis of ethynyl ketones have not found extensive application.

VI. HYDRATION OF POLYETHYNYL COMPOUNDS

The hydration of polyethynyl compounds has been investigated in fair detail. It is known[178,179] that in the presence of mercury(II) salts the addition of water to polyacetylenes takes place with participation of all the triple bonds and leads to the formation of a mixture of polyketones. However, as early as 1892, Griner[180] obtained by the hydration of hexa-2,4-diyne in the cold in the presence of aqueous sulphuric acid a substance to which he ascribed the structure of a β-ethynyl ketone (XXX):

$$CH_3C{\equiv}C{-}C{\equiv}C{-}CH_3 \rightarrow CH_3CO{-}CH_2C{\equiv}C{-}CH_3 .$$
(XXX)

Later Bohlmann et al.[181] established on the basis of the infrared spectra of the ketones and their hydrazones that the product of the addition of water to dimethyldiacetylene is an α-ethynyl ketone. Di-t-butylacetylene reacts with water slowly, probably due to steric hindrance. Under analogous conditions, the corresponding α-pentadiynyl ketone (XXXI) was obtained from octatriyne:

$$CH_3{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}CH_3 \xrightarrow[H_2SO_4]{H_2O} CH_3C{\equiv}C{-}C{\equiv}C{-}CO{-}C_2H_5 .$$
(XXXI)

When an attempt is made to hydrate tetra-acetylene, the latter breaks down completely. By hydrating asymmetric triacetylenes (XXXII), it is possible to form isomeric ethynyl ketones [(XXXIII) and (XXXIV)]:

$$(CH_3)_2CH{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}CH_3 \text{ (XXXII)} \rightarrow \begin{cases} (CH_3)_2CH{-}C{\equiv}C{-}CO{-}CH_2{-}CH_3 \text{ (XXXIII)} \\ (CH_3)_2CH{-}CH_2{-}CO{-}C{\equiv}C{-}CH_3 \text{ (XXXIV)} \end{cases} .$$

By analysing the NMR spectra of the hydration products of isopropylmethyldiacetylene, Petrov et al.[182] established that these are a mixture of compounds (XXXIII) and (XXXIV) with the latter predominating. It has been established chromatographically that the ketones (XXXIV) and (XXXIII) are formed in proportions of 9 : 1. Petrov et al. deduced a general rule governing the addition of water to asymmetric diacetylenes on the basis of the hyperconjugation effect of substituents, which varies in the series $CH_3 > CH(CH_3)_2 > C(CH_3)_3$.

The spreading of the hyperconjugation effect over a conjugated system, which determines the mode of addition, is respresented as follows:

$$CH_3{-}C{\equiv}C{-}C{\equiv}C{-}CH(CH_3)_2 .$$

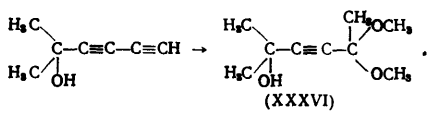
Consequently the hydration of isopropylmethyldiacetylene should involve preferentially the triple bond adjacent to the isopropyl group, since it is precisely this bond that has the highest electron density. Depending on the hydration conditions, diacetylenic hydrocarbons are capable of being converted into diketones and further into 2,5-disubstituted furans[183].

Gorn and Gorin investigated the hydration of diacetylene over a cadmium phosphate–calcium phosphate catalyst in the gas phase[184]. The liquid-phase hydration of diacetylene in an acid medium in the presence of mercury salts is known to result in the formation of diacetyl. German investigators[185] concluded that, together with diacetyl, another product is ethynyl methyl ketone (XXXV), which becomes wholly polymerised under the conditions of this reaction:

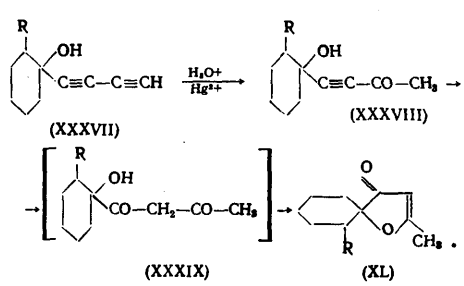
$$HC{\equiv}C{-}C{\equiv}CH \rightarrow [HC{\equiv}C{-}CO{-}CH_3] \rightarrow H_3C{-}CO{-}CO{-}CH_3 .$$
(XXXV)

The vapour-phase hydration of diacetylene yields the same results. The authors propose a hydration mechanism similar to that described above. They infer indirectly the intermediate formation of ethynyl methyl ketone from an appreciable amount of a polymeric deposit on the catalyst.

Acid-catalysed hydration may be used to synthesise ethynyl ketones with a monosubstituted triple bond. Sokolov and Petrov[186] obtained propionyl- and butyryl-acetylenes from penta-1,3-diyne and hex-1,3-diyne respectively. Water then adds to the triple bond adjacent to the alkyl substituent. On the other hand, the reaction of 5-methylhexa-1,3-diyn-5-ol with methanol in the presence of mercury salts results in the formation of the dimethylketal of 5-hydroxy-5-methylhex-3-yn-2-one (XXXVI):[187]


(XXXVI)

Volkov et al.[188] and Gusev et al.[189] studied the hydration of tertiary diacetylenic alcohols (XXXVII) in alkaline and acid media and the choice of conditions for the selective involvement of the triple bond of the alcohols (XXXVII) under the conditions of this reaction:

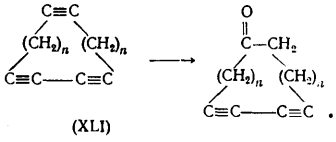

(XXXVII) (XXXVIII) (XXXIX) (XL)

Gusev et al.[189] found that the sole reaction products in an acid medium are the dihydrofuranones (XL) formed via the cyclisation of the intermediate β-diketones (XXXIX).

After a thorough study of the hydration of diacetylenic alcohols in an acid medium[188], it was concluded that the reaction takes place in stages. It is believed that the

principal primary products are ethynyl ketones (XXXVIII), which were isolated in good yields.

Under the conditions of Kucherov's reaction, macrocyclic triacetylenes (XLI) very readily combine with water at the isolated triple bond[190]; the hydration of the conjugated triple bonds requires more severe conditions:



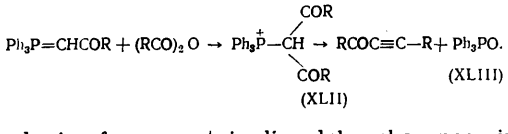
(XLI)

The hydration of acetylenes for preparative purposes is not particularly complicated and, if one remembers that at the present time there exist many methods for the synthesis of diacetylenic systems, one may hope that the above reaction will occupy an important place among the methods of synthesis of ethynyl ketones.

VII. OTHER SYNTHETIC METHODS

Apart from the general methods discussed in this review, there exist also many specific methods for the preparation of ethynyl ketones which are of value only in specific cases and have not found wide practical application.

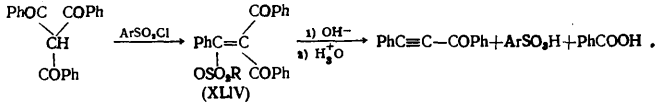
In recent years the intramolecular Wittig reaction has been widely used for the synthesis of various unsaturated compounds. Chopard et al.[191] used this method to prepare ethynyl ketones: on heating with acid anhydrides, stable phosphoranes with acyl substituents are acylated at the carbon atom adjacent to the phosphorus atom, forming diacylphosphoranes (XLII), the pyrolysis of which results in their conversion into ketones (XLIII) in high yields:



(XLII) (XLIII)

The pyrolysis of asymmetric diacylphosphoranes gives a mixture of ethynyl ketones. The yields of the desired products are 70–90%.

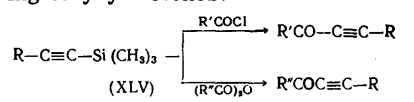
A novel method for the synthesis of ethynyl ketones was recently described by Brown and Harley-Mason[192]; under the action of an arenesulphonyl chloride, tribenzoylmethane is converted into the enolic ether (XLIV), which is converted by treatment with alkali in a dioxan–water mixture into phenylbenzoylacetylene and benzoic and arenesulphonic acids:



(XLIV)

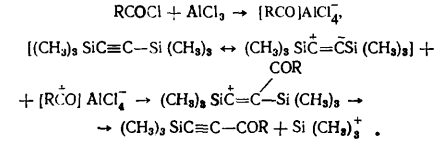
Bromobenzenesulphonyl and toluenesulphonyl chlorides may be used as the sulphonyl component.

We believe that the organosilicon synthesis of α-ethynylcarbonyl compounds by the method of Birkoffer[193] is promising. Bistrimethylsilylacetylene is known to be stable towards boiling water and alkali. Trimethylsilyl derivatives of hept-1-yne and hex-1-yne are also insensitive even to the action of inorganic acids. However, in the presence of aluminium chloride silylacetylenes (XLV) react with the chlorides and anhydrides of carboxylic acids, forming the corresponding ethynyl ketones:

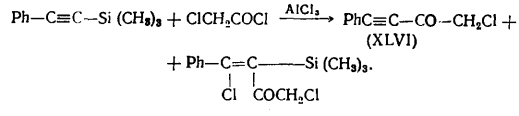


(XLV)

It is believed that the reaction has the following mechanism

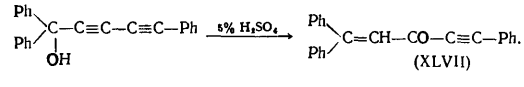


The synthesis is carried out at temperatures below 10°C in carbon disulphide or nitrobenzene. With the disilyl derivative of acetylene, only one trimethylsilyl group is replaced by an acyl residue. Usually the reaction takes place easily, ketones being formed in a yield of 40–90%. Only when chloroacetyl chloride is employed is the yield of the ketone (XLVI) reduced due to a side reaction involving its addition to the triple bond:



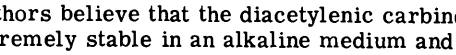
(XLVI)

Certain rearrangements of acetylenic carbinols leading to the formation of ketones undoubtedly merit attention. Thus, under the conditions of the Meyer–Schuster rearrangement, Cadiot and coworkers[194] obtained the ethynyl vinyl ketone (XLVII) from 1,1,5-triphenylpenta-1,3-diyn-5-ol:



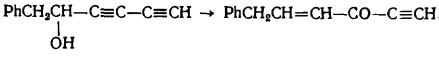
(XLVII)

In the alkaline hydrolysis of the acetates of secondary diacetylenic carbinols (XLVIII), ethynyl vinyl ketones (XLIX) are formed instead of the respective alcohols[195]:

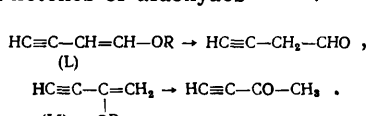


(XLVIII) (XLIX)

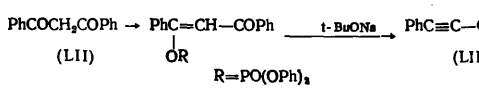
The authors believe that the diacetylenic carbinols formed are extremely stable in an alkaline medium and undergo a prototropic rearrangement. This hypothesis was confirmed by Kucherov[196]. On heating with a 3% alcoholic solution of potassium hydroxide, 6-phenylhexa-1,3-diyn-5-ol is readily converted into 6-phenylhex-3-en-1-yn-5-one:



The acid hydrolysis of alkoxyvinylacetylenes (L, LI) yields ethynyl ketones or aldehydes[197–200]:



Readily enolisable β-diketones (LII) can react smoothly with alcohols to form the corresponding enolic ethers[201], which are converted by alkaline hydrolysis into ethynyl ketones (LIII):[202]



(LII) (LIII)

Dibromotriphenylphosphorane is sometimes used as the esterifying agent[203] and the reaction is carried out in triethylamine:

$$PhCOCH_2COPh + Ph_3PBr_2 \rightarrow [PhC(OPPh_3)=CH-COPh]Br \rightarrow PhC\equiv C-COPh + Ph_3PO .$$

The interaction of diphenylketen with phenylethynylmagnesium bromide leads to the formation of ethynyl ketone (LIV):[204]

$$Ph_2C=C=O + PhC\equiv CMgBr \rightarrow Ph_2CH-CO-C\equiv C-Ph .$$

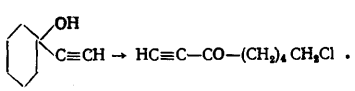
(LIV)

However, the reaction of diphenylketen with ethynylenedimagnesium dibromide led to a substance without the properties of ketones or the corresponding dienols[205].

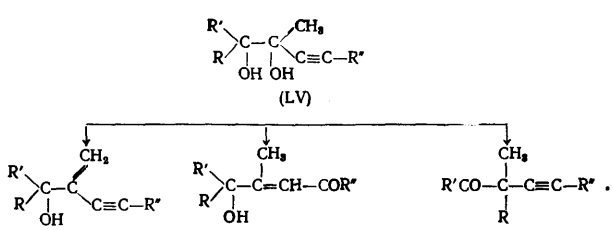
The method of synthesis of ethynyl ketones by the treatment of the sodium salt of acetylacetone with the chlorides of propiolic acids is noteworthy[206]:

$$PhC\equiv C-COCl + NaCH(COCH_3)_2 \rightarrow PhC\equiv C-CO-CH(COCH_3)_2 .$$

Good yields of monosubstituted ketones are quoted in a patent[207] where a method is proposed for the rupture of the cycloalkane ring in ethynyl alcohols with hypochlorous acid according to the following mechanism:

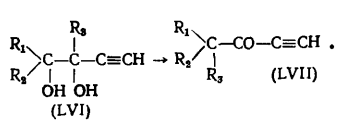


Recently a fairly detailed study was made of the isomerisation of various dihydroxyacetylenes to β-ethynyl ketones[208-215]. Numerous studies by Venus-Danilova and coworkers have been devoted to the elucidation of the reactions of acetylenic ditertiary α-glycols (LV) catalysed by sulphuric acid[210-214]. On heating with 20–40% sulphuric acid, these glycols are converted into compounds with the following structures:



(LV)

Usually the isomerisation takes place simultaneously via all three pathways. One of the reaction products is a β-ethynyl ketone. On the other hand, it has been stated that similar α-glycols (LVI) yield α-ethynyl ketones (LVII) after being passed over a dehydrating catalyst at 200–400 °C:[215]



(LVI) (LVII)

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Institute of Petroleum and Coal-based Chemical Synthesis at the Irkutsk Zhdanov State University, Angarsk

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The Chemistry of *O*-alkyl Derivatives of Lactams

R.G.Glushkov and V.G.Granik

The review gives a general account of the methods of synthesis and chemical properties of *O*-alkyl derivatives of lactams: lactim ethers, lactam acetals, and others. The reactions of *O*-alkyl derivatives of lactams with various nucleophilic and electrophilic reagents are described. Particular attention has been devoted to the possibility of using *O*-alkyl-lactams for the synthesis of various heterocyclic compounds which are of both chemical and biological interest. The bibliography includes 135 references.

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I. INTRODUCTION

The chemistry of *O*-alkyl derivatives of lactams (lactim ethers and lactam acetals) constitutes one of the least investigated branches of the chemistry of lactams in general. The lactams themselves have already been the subject of many investigations in various branches of organic chemistry. In particular extensive and interesting studies have been made on the chemistry of β-lactams [1] (with the aim of investigating the structure and synthesis of penicillins), reactions involving the incorporation of hydroxy- and aminoacyl-groups into lactams with conversion of the latter into the corresponding cyclols, cyclodepsipeptides, or cyclopeptides [2,3], and particularly on the development of methods for the synthesis of lactams for the preparation of various polymeric materials.

An attempt has already been made to give a general account of the available data on the chemistry of lactams as a specific class of heterocyclic compounds [4].

One of the most promising pathways in the development of the chemistry of lactams is the synthesis of various classes of organic compounds on the basis of lactams, associated with the preliminary activation of their amide function [5]. Activation of this kind of functional groups in various organic compounds has already yielded extremely interesting results. It is sufficient to point out that the conversion of ketones into enamines [6] or of acid amides into imino-ethers [7] made it possible to employ these compounds in new, hitherto unknown ways. Similarly the conversion of lactams into lactim ethers and lactam acetals gives rise to new possibilities in the application of lactams in organic synthesis.

The chemical properties of lactim ethers have already been the subject of two short reviews [8,9] but the latter cannot be regarded as sufficiently complete. Lactam acetals have begun to be studied only in recent years and these investigations have not been reviewed at all.

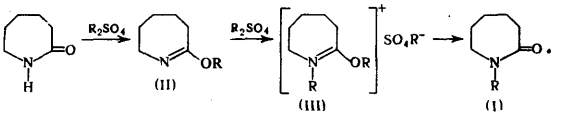
In the present review an attempt is made to give a general account of all the available data on the chemistry of *O*-alkyl derivatives of lactams in order to assess the advances in this field and the likely scope of the application of lactim ethers and lactam acetals in the synthesis of complex organic compounds.

One should also bear in mind that, apart from their use as starting materials for the synthesis of various organic compounds including dyes [10,11], lactim ethers are also of independent interest as biologically active materials [12] and also as accelerating agents in polymerisation processes [13].

II. METHODS OF SYNTHESIS OF LACTIM ETHERS

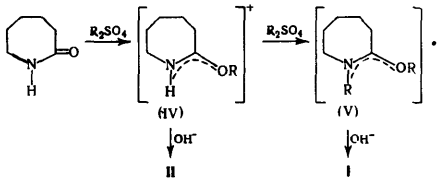
1. Direct Alkylation of Lactams

The methods for the preparation of lactim ethers by direct alkylation of lactams include the interaction of the latter with diazoalkanes [14] and also the alkylation of metal salts of lactams with alkyl halides [15]. Both methods are rarely used for the preparation of lactim ethers, since it is more convenient to use for this purpose the alkylation of lactams by dialkyl sulphates and trialkyloxonium fluoroborates. The alkylation of lactams by dialkyl sulphates was investigated in detail for caprolactam by Benson and Cairns [16], who established that this process depends to a considerable extent on the relative amounts of the components employed in the reaction. An excess of dialkyl sulphate leads, on the one hand, to a sharp reduction of the yield of lactim ethers due to the preferential formation of *N*-alkyl derivatives (I). On the other hand, the slow addition of an equimolar amount of an alkylating agent leads to an increase of the yield of *O*-alkylcaprolactim (II). The authors suggested that a considerable proportion of (I) is formed via compound (II) by the following hypothetical mechanism:



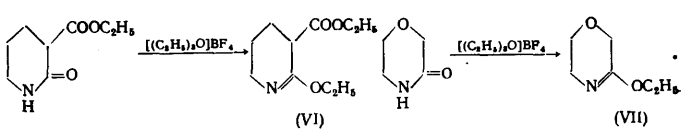
On the basis of the work of Bredereck and coworkers [17,18] on the reaction of acid amides with dimethyl sulphate, one may postulate that the ambidentate cation (IV) is formed

as an intermediate in this reaction and in the presence of an excess of dialkyl sulphate is alkylated further to the *NO*-dialkyl derivative (V). Under the influence of alkaline reagents, compounds (IV) and (V) are converted respectively into compounds (II) and (I). The conversion of compound (V) into (I) can also be achieved by heat treatment with elimination of dialkyl sulphate:

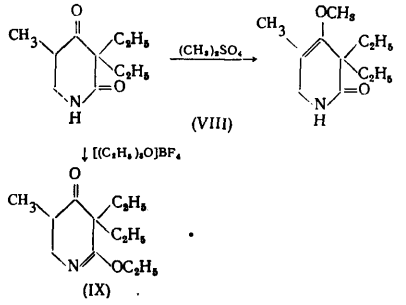


The method of Benson and Cairns is still used for the preparation of lactim ethers from the simplest lactams. However, recently another method of synthesis of lactim ethers has been acquiring increasing importance—alkylation of lactams by tertiary oxonium salts, in particular triethyloxonium fluoroborate [19,20]. This reaction involves the formation of an ambidentate cation, similar to the cation (IV), from which lactim ethers are also obtained by treatment with aqueous solutions of alkaline reagents. By virtue of their high electrophilicity, oxonium salts give better results than other alkylating agents [21].

It is noteworthy that in none of the numerous cases where equimolar amounts of trialkyloxonium fluoroborates were used to alkylate lactams [21-27] were *N*-alkyl derivatives isolated. This suggests the high selectivity of oxonium salts in such reactions. It is interesting that the high tendency towards *O*-alkylation under the action of triethyloxonium fluoroborate, compared with other alkylating agents, is shown also in the alkylation of keto-enols [28], the ambidentate ions of nitro-alkanes [29,30], and also potassium diethyl phosphorothioate [31]. Although special studies dealing with the comparison of the alkylating activities of dialkyl sulphates and trialkyloxonium fluoroborates have not as yet been published, nevertheless the available information suggests that tertiary oxonium salts provide a more univeral means for the synthesis of lactim ethers. Thus it has been noted that the attempts to alkylate 3-ethoxycarbonyl-2-piperidone [25] and 3-morpholinone [32] with dimethyl sulphate were unsuccessful, whereas the use of triethyloxonium fluoroborate resulted in high yields of 2-ethoxy-3-ethoxycarbonyl-3,4,5,6-tetrahydropyridine (VI) and 3-ethoxy-3,4-dehydromorpholine (VII):



The selective properties of triethyloxonium fluoroborate in the alkylation of lactams are shown particularly clearly in its interaction with 3,3-diethyl-5-methylpiperidine-2,4-dione (VIII) [25]. The interaction of compound (VIII) with an equimolar amount of dimethyl sulphate resulted in the alkylation of the carbonyl group in the 4-position, while in the reaction of compound (VIII) with triethyloxonium fluoroborate the corresponding lactim ether (IX) was obtained:



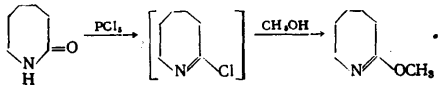
Recently a number of studies have been published on the alkylation of lactam with triethyloxonium fluoroborate when the ring contains, apart from the lactam group, also cyano-, ethoxycarbonyl, and acylated secondary amino-groups [25,33-41]. Selective alkylation of the lactam carbonyl was observed with formation of lactim ethers. In many cases when lactams were alkylated with triethyloxonium fluoroborate, the initial lactams were isolated as well as the lactim ethers, which is in all probability due to hydrolysis [analogous to the conversion of compound (V) into compound (I)] when the ambidentate cation, similar to the cation (IV), is attacked by the hydroxide ion during the isolation of the lactim ether.

Summarising, we may note that the use of triethyloxonium fluoroborate has real advantages over other alkylating agents both because of better yields of lactim ethers and because, when there is a choice between a possible attack on the lactam and other carbonyls, the former takes place preferentially (see above). This is also confirmed by the studies of Meerwein et al. [42], who classify carbonyl compounds in accordance with their capacity for alkylation by oxonium salts in the following series:

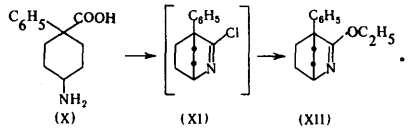
lactams > non-cyclic acid amides > lactones > carboxylic acid > esters > ketones > aldehydes.

2. Other Methods for the Synthesis of Lactim Ethers

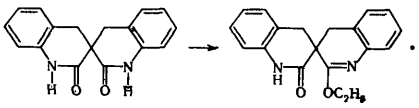
An important method for the preparation of lactim ethers consists in the conversion of lactams into the corresponding chlorinides followed by treatment with alcohols. Thus the interaction of caprolactam with phosphorus pentachloride and subsequent treatment of the reaction mixture with methanol led to the synthesis of *O*-methylcaprolactim [43]:



Similarly in the interaction of 4-amino-1-phenylcyclohexane-1-carbocyclic acid (X) with phosphorus pentachloride cyclisation takes place with formation of the chlorimide (XI), the alcoholysis of which yielded the lactim ether (XII) [44]:

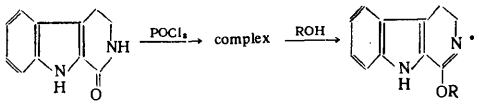


Similarly the interaction of the bishydrocarbostyryl-spirane (XIII) with phosphorus trichloride and phosphorus oxychloride followed by alcoholysis gave the corresponding lactim ether (XIV), which is also formed as a by-product in the reduction of di-(*o*-nitrobenzyl)malonic ester[45]:



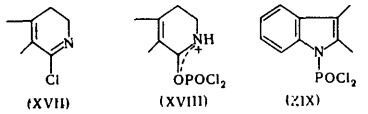
(XIII) (XIV)

Another example of the synthesis of lactim ethers from lactams and phosphorus oxychloride is the conversion of 3,4-dihydro-β-carbolin-1-one (XV) into 1-alkoxy-3,4-dihydro-β-carboline[46,47] (XVI):



(XV) (XVI)

Although the structure of the intermediate complex has not been accurately established, on the basis of the general properties of acid amides and lactams[48-52], one may suggest that, under the action of phosphorus oxychloride, the piperidone component of the molecule of compound (XV) is converted into compound (XVII) or (XVIII):

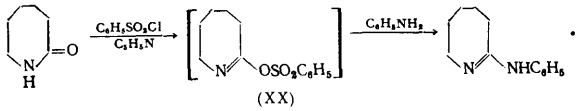


(XVII) (XVIII) (XIX)

However, one must remember that the indole component of the molecule is also capable of interacting with $POCl_3$ to form the phosphoramidic dichloride (XIX)[33].

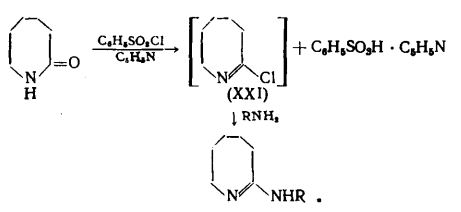
The reaction of the simplest lactams with benzenesulphonyl chloride probably takes place similarly as the reaction of β-carbolin-1-one (XV) with phosphorus oxychloride.

In their study of the synthesis of cyclic amidines from lactams, Oxley et al.[53] proposed a mechanism according to which, on treatment with benzenesulphonyl chloride in the presence of pyridine, caprolactam is converted into the intermediate *O*-benzenesulphonate of the caprolactim (XX), which readily reacts with amines, forming cyclic amidines:



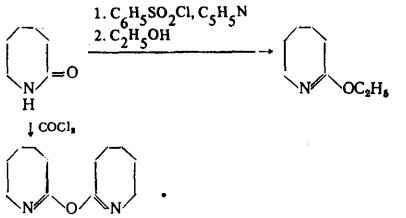
(XX)

However, later, in connection with the development of the synthesis of αβ-pentamethylenetetrazole[54], a detailed study of the first stage of this mechanism showed that this hypothesis is incorrect, since a high yield of the salt of benzenesulphonic acid and pyridine and not pyridinium chloride was isolated from the reaction mixture. Therefore a different mechanism was put forward, postulating the intermediate formation of the chlorimide of the caprolactam (XXI):



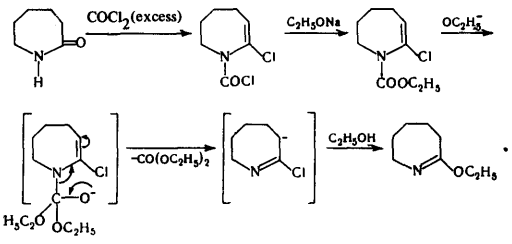
(XXI)

It is noteworthy that the intermediate chlorimide is extremely labile and is readily hydrolysed to caprolactam, all attempts to isolate it proving unsuccessful. This last study suggests that the syntheses of lactim ethers based on the interaction of lactams with reagents such as benzenesulphonyl chloride, chlorocarbonic ester, and phosgene[55-57] also probably takes place via the intermediate formation of chlorimides:

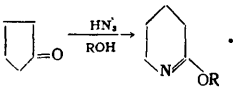


The interaction of sulphonyl chlorides with cycloalkanone oximes in pyridine probably also takes place similarly. In the first stage of this reaction the oxime evidently undergoes the Beckmann rearrangement and the lactam formed is converted into the chlorimide, from which the corresponding lactim ether is obtained by reaction with alcohol[58].

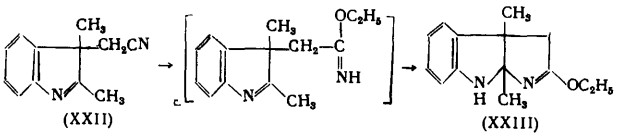
Tetenbaum's study[59] of the interaction of caprolactam with phosgene and the alcoholysis of 2-chloro-1-chlorocarbonyl-4,5,6,7-tetrahydro-1*H*-azepine also demonstrates the possibility of synthesising lactim ethers via the intermediate formation of compounds containing the chlorimide N=C–Cl group:



Among other methods of synthesis of lactim ethers, mention should be made of the procedure which consists in the interaction between cyclic ketones and hydrazoic acid in the presence of alcohol[60]:

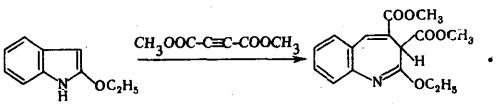


Apart from the general methods for the synthesis of lactim ethers described above, the ethers can also be obtained using the individual properties of particular organic compounds. An example is provided by the conversion of 3-cyanomethyl-2,3-dimethylindolenine (XXII) into the tricyclic lactim ether (XXIII)[61] under the influence of a solution of sodium ethoxide or hydrogen chloride in alcohol. In particular, in this case use was made of the capacity of indolenines to react with imines at the 2-position of the indolenine molecule:



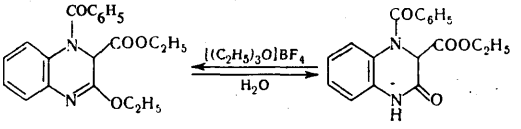
(XXII) (XXIII)

Mention can also be made of the synthesis of a lactim ether by the expansion of the indole ring to a benzazepine ring by the mechanism[62]:

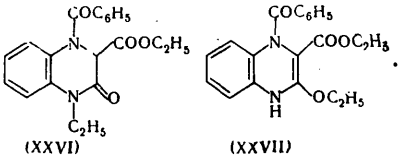


III. CHEMICAL PROPERTIES AND REACTIONS OF LACTIM ETHERS

Lactim ethers are extremely reactive towards nucleophilic agents, which readily distinguishes them from *N*-alkyl-lactams and other isomeric compounds. One may quote as an example the lactim ether derived from 4-benzoyl-3-ethoxycarbonyl-1, 2, 3, 4-tetrahydro-2-quinoxalinone (XXIV)[63]. The reaction of triethyloxonium fluoroborate with 4-benzoyl-3-ethoxycarbonyl-1, 2, 3, 4-tetrahydro-2-quinoxalinone (XXV) yielded a substance to which one of the following three isomeric structures (XXIV), (XXVI), or (XXVII) could be ascribed, bearing in mind the possibility to alkylation with transfer of the reaction centre:



(XXIV) (XXV)

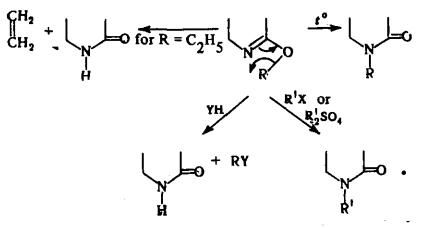


(XXVI) (XXVII)

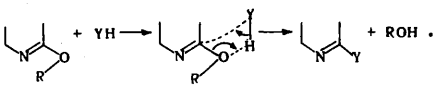
On the basis of infrared and NMR spectroscopic data, the structure (XXVII) was eliminated. However, the spectroscopic data did not allow an unambiguous choice between structures (XXIV) and (XXVI). Therefore the compound obtained was hydrolysed under exceptionally mild conditions (in water at 20°C) which gave an almost quantitative yield of the initial lactam (XXV). Such mild hydrolysis conditions undoubtedly indicate that the compound obtained is a lactim ether, this being confirmed subsequently also by its reactions (see below).

The reactions of lactim ethers with participation of the lactim ether group can be divided into two principal classes.

1. Reactions accompanied by the elimination of the *O*-alkyl residue and the formation of lactam derivatives:

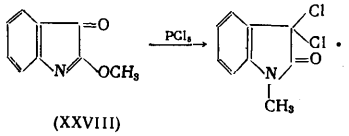


2. Reactions involving the lactim carbon atom with elimination of the alkoxy-group:



Reactions of the first type include the thermal rearrangement of lactim ethers into *N*-alkyl-lactams. In particular it was noted that 2-methoxy-3-oxoindolenine (XXVIII) undergoes on heating thermal isomerisation to *N*-methylisation[64]. In the paper by Benson and Cairns[16] mentioned above, a similar conversion of *O*-methyl(ethyl)caprolactim into the *N*-methyl(ethyl) derivative was described.

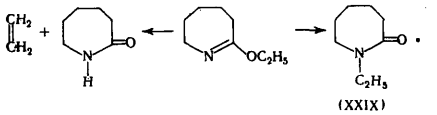
Another example of this type of rearrangement is the interaction of the lactim ether derived from isatin (XXVIII) with phosphorus pentachloride, which is also accompanied by the substitution of the oxo-group in the 3-position by two chlorine atoms[66]:



(XXVIII)

According to many investigators[16,65], this rearrangement is a common property of lactim ethers, similar to the analogous rearrangement of the simplest imino-ethers[7].

New data on this problem were obtained by Ralls and Eliger[67] in a study of the thermal isomerisation of *O*-ethylcaprolactim. In this investigation it was shown that the lactim ether remains unchanged at 193°C and only after prolonged heating (21 h at 237°C) is a small amount converted into *N*-ethylcaprolactam. The principal reaction product is caprolactam formed from the lactim ether on elimination of ethylene:

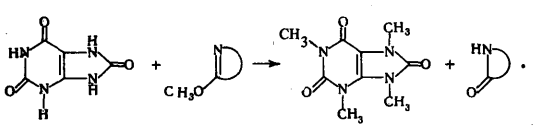


(XXIX)

The authors suggested that the rearrangement of the lactim ether into *N*-ethylcaprolactam (XXIX) is caused by traces of dialkyl sulphate and demonstrated this by the heat treatment of *O*-ethylcaprolactim in the presence of diethyl sulphate; the *N*-alkyl derivative (XXIX) was isolated as the main product. Similar behaviour was observed also with *O*-methylvalerolactim[67].

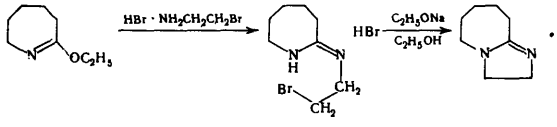
The need for the presence of dialkyl sulphate in the rearrangement of lactim ethers into *N*-alkyl-lactams is also consistent with the finding that similar isomerisation was achieved earlier in the interaction between *O*-methylcaprolactim and dimethyl sulphate[16]. The process probably involves the intermediate formation of compound (V) (see Russ. p. 914).

Reactions of the first type include also alkylation by lactim ethers of compounds with definite acid properties. Thus lactim ethers have been used as alkylating agents in reactions with compounds containing imino-groups[68], such as uric acid, xanthines, and hypoxanthines, and also for the esterification of organic acids[69]:

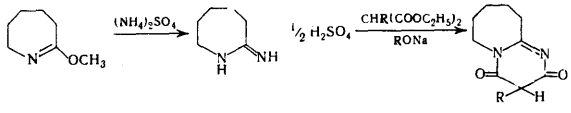


Among reactions of the second type the most common and probably the most promising for the synthesis of heterocyclic systems are reactions with various amino-derivatives and also with compounds having active methylene groups.

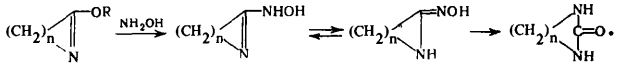
The synthesis of amidines from lactim ethers and amines takes place very readily and with high yields [8,9,16,21,70-76]. As an example, one may quote the synthesis of derivatives of imidazo[1,2-*a*]azepines carried out by Stolle et al.[77] by the reaction of *O*-ethylcaprolactim with β-bromoethylammonium bromide followed by cyclisation under the action of sodium ethoxide of the resulting β-bromoethylamidine derived from the caprolactim:



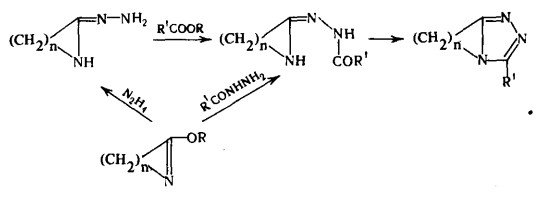
and also the synthesis of derivatives of pyrimidino[1,2-*a*]-azepines from *O*-methylcaprolactim[70]:



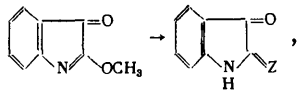
Lactam oximes have been synthesised by the interaction between lactim ethers and hydroxylamine [9,72,73,78]. This reaction became particularly important after it had been established that, under the influence of polyphosphoric acid, lactam oximes undergo the Beckmann rearrangement with formation of polymethyleneureas[79]:



The reaction of lactim ethers with hydrazine hydrate and substituted hydrazines [5,54,76,80-82] takes place even more readily because of the even more pronounced nucleophilic properties of the latter reagents. The "hydrazidines" formed in this process are extremely active and can take part in various cyclisations involving the amino-group of the side chain and the ring nitrogen. Thus, when the hydrazine of caprolactim was treated with nitrous acid, αβ-pentamethylenetetrazole (corazole) was synthesised [54,80,81], while the syntheses employing hydrazidines derived from other lactim ethers gave analogues of this compound [32,35]. It should also be mentioned that polymethylenetetrazoles may be synthesised by the action of an excess of hydrazoic acid on lactim ethers[83] as well as by the reaction of this acid with *O*-acyl-lactims (or lactam chlorimides) obtained from lactams and sulphonyl chlorides or phosphorus oxychloride[84]. Other possibilities which arise when similar "hydrazidines" are obtained may be demonstrated using as an example their conversion into polymethylenetriazoles [85-87]:



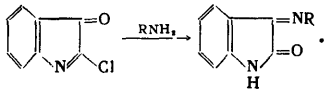
The reactions of the lactim ether of isatin (XXVIII) with amines, hydroxylamines, and substituted hydrazines [76,88] require special consideration. When compound (XXVIII) reacts with the above reagents, the condensation involves only the lactim ether group but not the oxo-group:



(XXVIII)

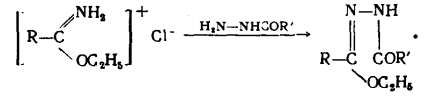
where Z = RN^-, $RNH-N^-$, or $-N-OH$.

From this, one may conclude that the lactim ether group in compound (XXVIII) is extremely reactive. We may also mention that the lactim ether group in this compound is probably even more reactive than the chlorimide group. Thus, it has been stated that, under the action of tosylhydrazine and aniline on isatin chlorimide, the oxo-group in the 3-position is attacked; the reaction is accompanied by the hydrolysis of the chlorimide to the lactam[89]:



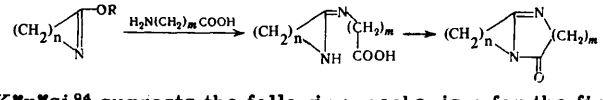
The reactions of lactim ethers with semicarbazides, thiosemicarbazides, and sulphonyl hydrazides as a rule stop at the amidrazone stage.

It is interesting that the reaction of aliphatic imino-ethers with the above components take place by a completely different mechanism: not with the elimination of alcohol and the formation of a C=N bond, but with the dissociation of the C=N bond and the elimination of ammonia [90-92]:

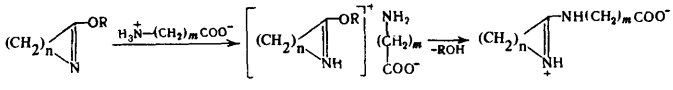


The reactions of lactim ethers with amino-acids have been investigated in fair detail [21,23,93]. It has been established that these reactions take place very readily, substituted amidino-acids, the cyclisation of which leads to various condensed dihydropyrimidines or imidazolines, being formed.

The cyclisation of aliphatic amino-acids requires fairly severe conditions, while with aromatic or heterocyclic amino-acids, where a fairly high degree of aromatisation of the diazine ring is attained, the process takes place readily so that the intermediate amidines cannot be isolated:



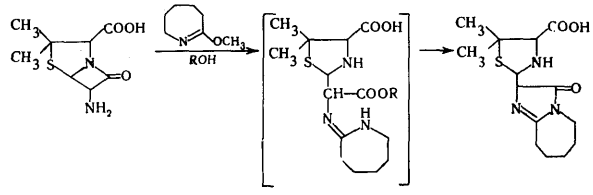
Körösi[94] suggests the following mechanism for the first stage of this process:



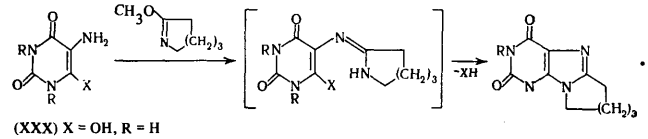
According to this mechanism, the reaction begins with the protonation of the lactim nitrogen, which is achieved more readily when the acid properties of the amino-acid carboxyl are enhanced (i.e. in the case of aromatic and heterocyclic amino-acids). The protonation of the lactim nitrogen increases the electrophilicity of the adjacent carbon atom and is responsible for the ease of the subsequent nucleophilic substitution of this atom. Consequently, when lactim ethers are condensed with amines, account must be taken not only of the basicity of the initial amines but also of the possibility of the formation of a salt by the lactim ether group.

The reactions of lactim ethers with amino-acid esters[95] lead to the corresponding amidino-acid esters. The principal factor which determines the course of this process is the basicity of the amino-group, which is clearly illustrated, for example, by the condensation of lactim ethers with the aminocrotonic ester, which either does not occur at all[21,95], or takes place with a relatively low yield[70].

The interaction of *O*-methylcaprolactim with 6-aminopenicillanic acid takes place with the opening of the β-lactam ring and subsequent cyclisation of the derivative of penicilloic acid involving the ester group and the endocyclic nitrogen of the azepine ring[96]:

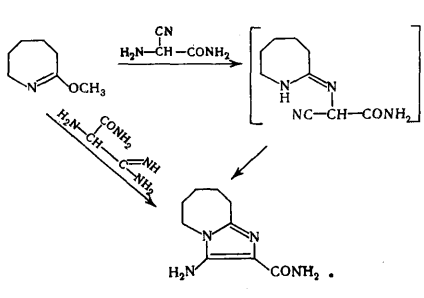


The ease of formation of amidines in the reactions of lactim ethers with amines was used in the synthesis of 8,9-polymethylenepurines. The attempts to condense *O*-methylcaprolactim with uramil (XXX) and 4,5-diamino-1,3-dimethyluracil (XXXI), undertaken to obtain 8,9-pentamethylenexanthine showed that lactim ethers do not react with 5-aminouracil derivatives, probably because of the low basicity of their amino-groups:



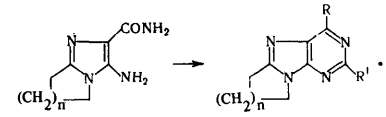
(XXX) X = OH, R = H
(XXXI) X = NH_2, R = CH_3

The synthesis of 1,2-polymethylene derivatives of 5-amino-4-carbamoylimidazoles, which are key compounds in the synthesis of 8,9-polymethylenepurines, was achieved by condensing lactim ethers with α-amino-α-cyanoacetamide. It was found that, despite the presence of an active methine unit in the latter compound, the reaction involves selectively the amino-group, as shown by the physicochemical properties of the products, further reactions, and, in the case of *O*-methylcaprolactim, also by synthesis—the condensation of the caprolactim with the dihydrochloride of α-amidino-α-aminomalonamide[97]:



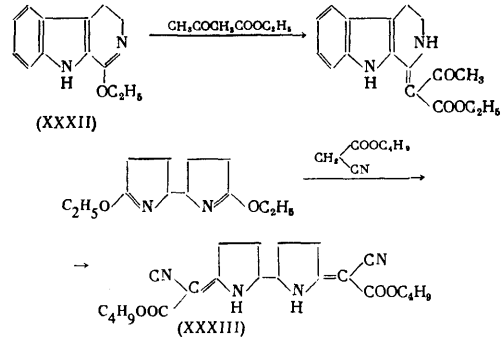
When this reaction was extended to butyro- and valerolactims, it was found[98] that an additional enhancement of the electrophilicity of the attacking carbon atom of the lactim group is necessary, and this was achieved by carrying out the reaction in alcohol containing catalytic amounts of hydrogen chloride.

The reaction of lactim ethers with α-amino-α-cyanoacetamide thus developed permitted the synthesis of a group of polymethyleneimidazoles and made it possible to convert the latter into 8,9-polymethylenepurines:



The general features of this reaction have also been compared using more complex examples such as 1-ethoxyisoindolenine[24] and also lactim ethers containing an additional hetero-atom in the lactam ring[32,35,99]. When α-amino-α-cyanoacetamide was condensed with lactim ethers derived from 3-morpholinone[32], 3-thiazanone[99], and 2-piperazinone[35], it was shown that the introduction of a second hetero-atom in the 4-position of the lactam ring does not alter significantly the reactivity of lactim ethers.

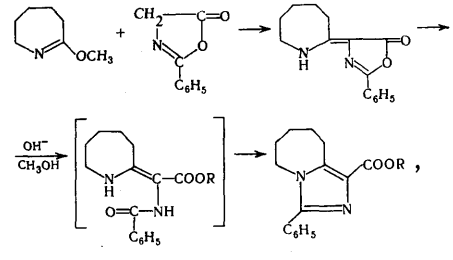
The high reactivity of lactim ethers is shown particularly clearly in their capacity to form a new carbon–carbon bond in the reaction with compounds containing active methylene groups, such as acetoacetic, cyanoacetic, and malonic esters and their derivatives, acetylacetone, barbituric acid, rhodanine, nitromethane, oxindole, and others[8,9,33,100–102]. One may quote as examples the condensation of the lactim ether derived from 3,4-dihydro-β-carbolin-1-one (XXXII) with acetoacetic ester[103] and also the condensation of the bislactim ether derived from 2,2′-di-5-pyrrolidone (XXXIII) with butyl cyanoacetate[26]:



(XXXII)

(XXXIII)

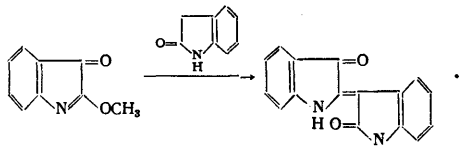
Another example of the reaction of lactim ethers with compounds having an active methylene group is the condensation of *O*-methylcaprolactim with 2-phenyl-5-oxazolone[104] which leads to the synthesis of 3,4-pentamethyleneimidazoles via the intramolecular rearrangement of the intermediate 2-phenyl-4-(2′-homopiperidylene)-5-oxazolone:



where R = H or CH_3.

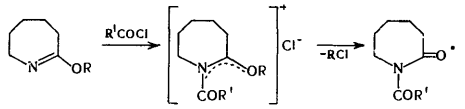
The condensation of the lactim ether derived from isatin (XXVIII) with oxindole in an anhydrous medium (benzene, acetic anhydride) in the presence of a catalytic

amount of concentrated sulphuric acid involves the active α-methylene unit with formation of indirubin (XXXIV)[102]:

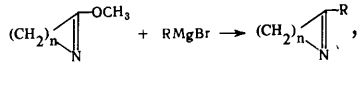


(XXVIII) (XXXIV)

In the literature there are contradictory data on the interaction between lactim ethers and acid chlorides. In 1956 a patent was published in which it is stated that this interaction leads to the corresponding *O*-acyl-lactams[105]. In another study on this problem[106] it was shown for a large number of examples, using spectroscopic methods, that the reaction products are *N*-acyl-lactams:

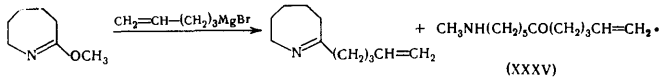


Numerous studies have been made on the interaction between lactim ethers and Grignard reagents[72,73,107-112]. It has been stated that this reaction depends on the size of the lactam ring. Thus, whereas *O*-methylbutyro- and *O*-methylvalero-lactims give bases of the same type:



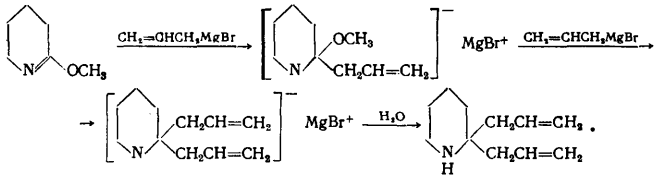
(*n* = 2,3)

in the case of *O*-methylcaprolactim, in addition to similar bases, *N*-methylaminoketones of type (XXXV) are sometimes formed, which can be explained by the conversion of *O*-methylcaprolactim into *N*-methylcaprolactam and subsequent interaction of the latter with a Grignard reagent[109]:

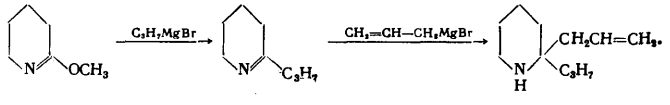


(XXXV)

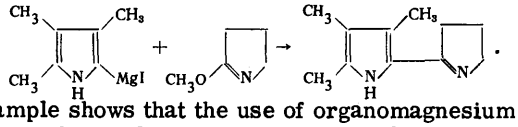
In the general case (where R in RMgX is a simple alkyl or aryl) it is suggested that the reaction does not take place via the addition of the Grignard reagent to the C=N bond but involves the direct substitution of the alkoxy-group of the lactim ether by the alkyl residue. In this connection, the reaction of *O*-methylvalerolactim with allylmagnesium bromide constitutes an unusual case[112]. This reaction yields only the gem-derivative, which is probably due to the addition of the Grignard reagent to the C=N bond:



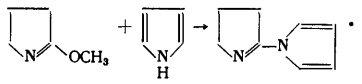
This mechanism is consistent with the capacity of allylmagnesium bromide to add to the double bond of 2-propyl-3,4,5,6-tetrahydropyridine:



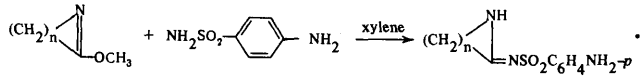
An interesting example of the reaction of lactim ethers with organomagnesium compounds is the synthesis of 2,2′-pyrrolylpyrrolines[108]:



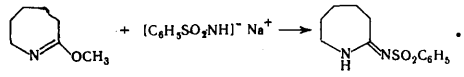
This example shows that the use of organomagnesium derivatives of pyrrole makes possible condensation involving the α-position of the pyrrole ring. When pyrrole itself reacts with the lactim ether, the condensation involves the pyrrole nitrogen with formation of a C–N bond[113]:



Sulphonamides enter into a similar condensation with lactim ethers and in the presence of an aromatic amino-group and a sulphonamide group the reaction of the lactim ether involves preferentially the sulphonamide group[114]:

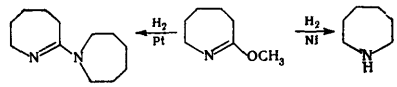


The interaction of lactim ethers with ammonium benzenesulphonate leads to the corresponding amidine salt and that with sodium benzenesulphonate yields the benzenesulphonyl derivative of amidinocaprolactim[71]:



An important property of lactim ethers is the relative (compared with lactams) ease of their reduction to cyclic imines. The reduction of lactams involves considerable difficulties and is as a rule carried out with lithium aluminium hydride. In this connection, the comparatively easy hydrogenation of lactim ethers is promising[16,72,109].

The studies of Benson and Cairns[16] showed that the hydrogenation of *O*-methyl and *O*-ethylcaprolactims over Raney nickel, ruthenium oxide, and the barium–copper–chromite catalyst give high yields of hexamethyleneimine. When platinum is used in this case, an amidine is formed by the mechanism:

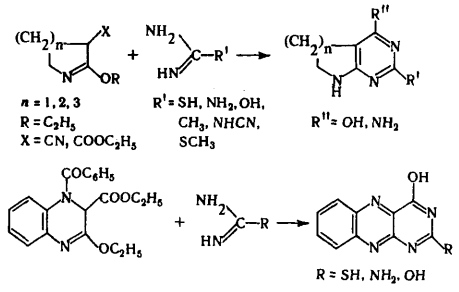


The catalytic hydrogenation of *O*-methylvalerolactim over platinum oxide yielded piperidine[109] and the hydrogenation of *O*-methylbutyrolactim over platinum in acetic acid resulted in the formation of pyrrolidine[72]. In addition, the reduction of lactim ethers with lithium aluminium hydride has also been described—cyclic imines were obtained in all cases[109].

So far we have considered the reactions of monofunctional lactim ethers involving mainly their imino-ether group. In such cases new heterocyclic rings are formed from the carbon and nitrogen of the lactim ether group.

Recently a number of studies have been published, in which di- (or tri-) functional lactim ethers were used for this purpose[25,38-41,115]. The first example of this type of synthesis was the interaction of the lactim ether derived from 3-ethoxycarbonyl-2-piperidone (XXXVI) with thiourea in the presence of an alcoholic solution of sodium ethoxide[25]. A detailed study of this reaction was carried out for

lactim ethers derived from 3-ethoxycarbonyl-2-piperidone (XXXVI), 3-cyanocaprolactam (XXXVII), 3-ethoxycarbonylcaprolactam (XXXVIII), 3-ethoxycarbonyl-2-pyrrolidone (XXXIX), and ethoxycarbonyl-4-benzoyl-1,2,3,4-tetrahydro-2-quinoxalinone (XL) [35-38,40,115].



It was shown that this reaction constitutes a general synthesis of condensed pyrimidines and that the pyrimidine cyclisation depends both on the structure of the lactim ethers and on the properties of the "amidine" component. The use of guanidine and thiourea as the "amidine" component gives the best results in all cases of the synthesis of the corresponding condensed pyrimidines. It is noteworthy that, whereas in the condensation of compounds (XXVIII)–(XL) with urea condensed uracils were obtained in a low yield, in a similar condensation of compound (XXXVI) hydrogenated 2,4-dihydroxypyrido[2,3-*d*]pyrimidine was obtained in a satisfactory yield, comparable to that of the product obtained in the reaction of compound (XXXVI) with acetamidine.

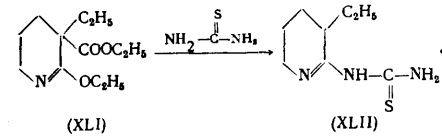
The reactivity of other "amidine" components is as a rule intermediate between the above extremes and the components can be arranged in the following sequence:

guanide ≃ thiourea > cyanoguanidine > acetamidine > *S*-methylisothiourea > urea.

If one disregards the anomalously low yields when *S*-methylisothiourea is used, then the relative reactivities of the amidine components in the above series are the same as in the usual pyrimidine cyclisations [116-119]. Furthermore the condensation of lactim ethers derived from 3-ethoxycarbonyl-lactams with amidine components greatly depends on the stability of the reactants, as in the analogous reaction of malonic esters [120].

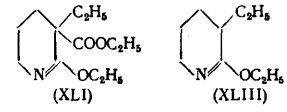
Like aliphatic imino-ethers, lactim ethers are very labile both in acid and alkaline media. Therefore the reaction depends in many respects on the relative rates of the main process (pyrimidine cyclisation) and the side reactions associated with the instability of the starting materials. When the "amidine" components are substances with high basicity and high capacity for enolisation under the process conditions, pyrimidine cyclisation predominates and the yields of the condensed pyrimidines are high. On the other hand, when the "amidine" components do not have these properties (or have them to a much smaller extent), the lactim ethers are probably alcoholysed to lactams with subsequent rupture of the lactam ring [121]. Comparison of the reactivities of the lactim ethers derived from 3-cyano- and -3-ethoxycarbonyl-caprolactams shows that, as in the usual pyrimidine cyclisations [120], the latter are more reactive. Whereas the condensation of the lactim ether derived from 3-cyanocaprolactam with urea does not occur at all, in the condensation of the 3-ethoxycarbonyl derivative condensed uracil was obtained, albeit in a low yield.

The use of bifunctional lactim ethers in the synthesis of condensed pyrimidines made it possible to achieve the synthesis of a new heterocyclic system—pyrimido[4,5-*b*]-tetrahydroazepine [36,37] and also to develop new methods for the synthesis of alloxazines [41], 7*H*,5,6-dehydropyrrolo[2,3-*d*]pyrimidines [38,39], and 8*H*,piperidino[2,3-*d*]pyrimidines [25,115]. A further development of these studies was the investigation of the condensation of the lactim ether derived from 3-ethoxycarbonyl-3-ethyl-2-piperidone (XLI) with thiourea, guanidine, and other amidine components [115]. The aim was to synthesise condensed piperidino[2,3-*d*]-pyrimidines with an angular ethyl group, which are cyclic analogues of the biologically active 5,5-disubstituted barbituric acids. The study of the interaction of compound (XLI) with thiourea showed that the condensation does not occur when an equimolar amount of sodium alkoxide is employed, while in the presence of an excess of this reagent *N*-(3-ethyl-3,4,5,6-tetrahydropyrid-2-yl)thiourea (XLII) was isolated:



(XLI) (XLII)

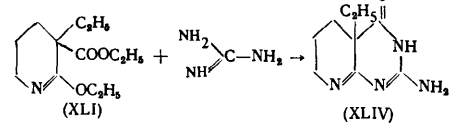
The above mechanism shows that in this reaction the ethoxycarbonyl group is eliminated, probably as a result of its alcoholysis with formation of diethyl carbonate, as was observed earlier for disubstituted cyanoacetic esters in the synthesis of iminobarbituric acids [122,123]. Comparison of the reactivities of the lactim ethers (XLI) and (XLIII) shows that the former should be more reactive in nucleophilic substitution reactions than compound (XLIII) because of the negative inductive effect of the ethoxycarbonyl group and the associated higher partial positive charge on the "lactim" carbon atom:



(XLI) (XLIII)

On this basis, one may suppose that the first stage in this process is attack by thiourea on the "lactim" carbon atom and consequently the lactim ether group is more reactive under the conditions of this reaction than the ethoxycarbonyl group. The need for an excess of sodium hydroxide in this reaction is probably due to the low dissociation constant of thiourea.

The interaction of compound (XLI) with guanidine, which is a stronger base, now leads to the product of cyclisation involving the ethoxycarbonyl group, 2-amino-4-hydroxy-10-ethyl-4,5,6,7,8,10-hexahydropyrido[2,3-*d*]pyrimidine (XLIV) with an angular alkyl group in the 10-position of the bicyclic compound being formed. In this case the yield is lower than in the condensation of compound (XXXVI) with guanidine, which can probably be accounted for by the incomplete aromatisation of the pyrimidine ring in compound (XLIV):



(XLI) (XLIV)

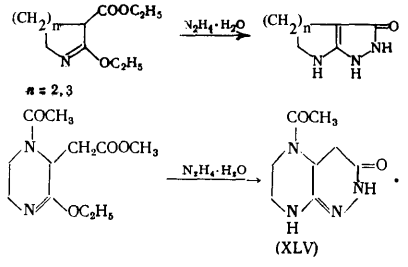
The last factor is evidently decisive in cyclisations of this type, involving the formation of a diazine ring. This is also confirmed by the fact that the attempts to condense

the lactim ether derived from 4-acetyl-3-methoxycarbonylmethyl-2-piperazinone with "amidine" components proved to be unsuccessful[40].

It is striking that the reaction of compound (XLI) with urea does not occur at all, probably because of the lower tendency of the latter to enolise under the reaction conditions compared with thiourea[113]. In all these cases one should also bear in mind the slightly reduced reactivity of the lactim ether group of compound (XLI) compared with compound (XXXVI) in consequence of the electron-donor effect of the alkyl group in the 3-position of the lactam ring.

In this connection it is also interesting to note that the reduced reactivity of compound (XLI) compared with compounds (XXXVI)–(XL) is confirmed by its higher stability to alcoholysis under the conditions of condensation with "amidine" compounds, since, in contrast to compounds (XXXVI)–(XL), compound (XLI) is partially regenerated in almost all cases.

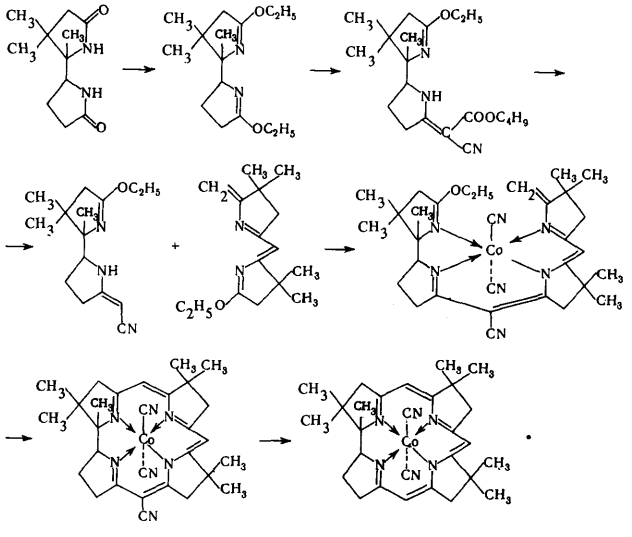
The condensation of bifunctional lactim ethers with "amidine" reagents does not exhaust the vast possibilities created by these compounds for the synthesis of various heterocycles. As an illustration, one may quote the condensations of certain lactim ethers with hydrazine hydrate, giving condensed pyrazoles[25,37] and pyridazines[40]:



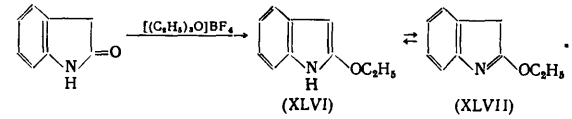
(XLV)

The "amidine" structure of compound (XLV) was demonstrated by infrared and NMR spectroscopy.

The high reactivity of lactim ethers made it possible to use these compounds in the study of the synthesis of complex organic compounds such as representatives of the corrin system[124-127]. As an example, one may quote the synthesis of racemic dicyano(1,2,2,7,7,12,12-heptamethylcorrin)cobalt (III)[125]:

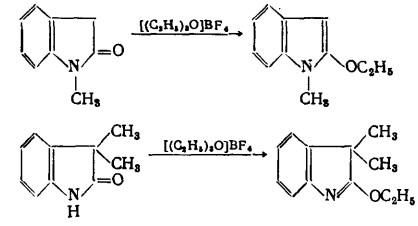


The ethylation of oxindole and its derivatives with triethyloxonium fluoroborate occupies a special place in the chemistry of lactim ethers. Harley-Mason and Leeney[22] established that the interaction of oxindole with triethyloxonium fluoroborate yields 2-ethoxyindole (XLVI) which isomerises on sublimation to the lactim ether (XLVII) derived from oxindole. When the latter is heated above the melting point, the reverse conversion of compound (XLVII) into compound (XLVI) can be achieved:



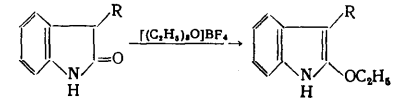
(XLVI) (XLVII)

2-Ethoxy-1-methylindole and 2-ethoxy-3,3-dimethylindolenine were prepared as models for the investigation of these reactions:



The study of the NMR and infrared spectra of the compounds obtained and their comparison with the spectra of the model compounds convincingly demonstrated the occurrence of the tautomerism (XLVI) ⇌ (XLVII).

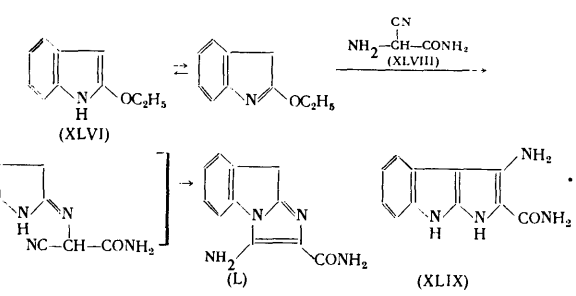
In another study an attempt was also made to obtain the lactim ether derived from oxindole (XLVII) and 3-ethoxycarbonylindole[33]. However, in both cases indole and not indolenine derivatives were isolated:



where R = H or $COOC_2H_5$.

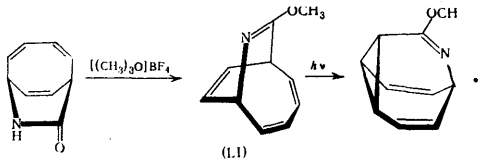
Bearing in mind the capacity of compound (XXXVI) for isomerisation to compound (XLVII), the capacity of lactim ethers to condense with α-amino-α-cyanoacetamide (XLVIII), and also the capacity of the α-alkoxy-derivatives of certain enamines for nucleophilic substitution of alkoxy-groups[128], an attempt was made in this investigation to condense compound (XLVI) with compound (XLVIII) in alcohol in the presence of catalytic amounts of hydrogen chloride.

A detailed study of the physicochemical properties of the product and in particular its NMR spectrum, showed that it is not 3-amino-2-carbamoyl-pyrrolo[2,3-*b*]indole (XLIX) but the "normal" product of the reaction of lactim ethers with compound (XLVIII)—3-amino-2-carbamoylimidazo[1,2-*a*]indoline (L). This process may be represented by the following mechanism:



(XLVI) (L) (XLIX)

Together with high reactivity in relation to nucleophilic reagents, the lactim ether group is sufficiently stable to achieve certain sometimes very complex reactions. As an illustration one may quote the isomerisation of the lactim ether (LI) in which the lactim ether group is preserved[27]:

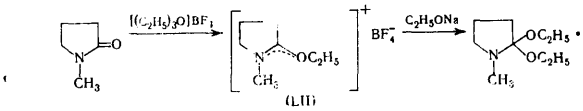


(LI)

IV. METHODS OF SYNTHESIS AND CHEMICAL PROPERTIES OF OTHER *O*-ALKYL DERIVATIVES OF LACTAMS

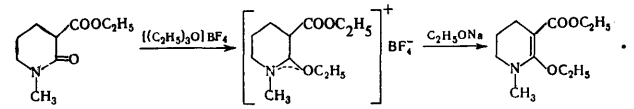
The activation of the amide group in lactams by their conversion into lactim ethers greatly extended the range of applications of lactams and made it possible to synthesise examples of various classes of organic compounds. However, the above reactions are always subject to a constant limitation in the choice of the lactam, since in the synthesis of lactim ethers only lactams unsubstituted at the nitrogen atom must be employed.

A further extension of the application of *O*-alkyl derivatives of lactams in organic chemistry was achieved in the study of a new branch of lactam chemistry—that of lactam acetals[50,129-132]. Lactam acetals were synthesised for the first time by Meerwein and coworkers[130,131] by the alkylation of *N*-substituted lactams with triethyloxonium fluoroborate, followed by the decomposition of the resulting fluoroborate complex (LII) with sodium ethoxide:

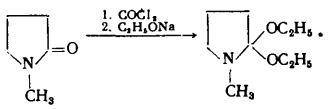


(LII)

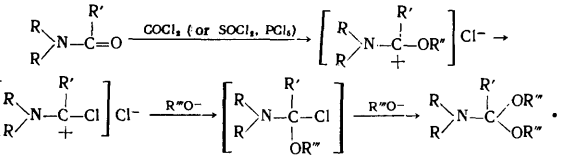
In the presence of an electron-acceptor substituent in the 3-position of the lactam ring, the decomposition of the intermediate fluoroborate complex by sodium ethoxide is accompanied by the elimination of a proton from the 3-position and the formation of a 2,3-dehydro-derivative, as happens, for example, in the case of 3-ethoxycarbonyl-*N*-methyl-2-piperidone[133]:



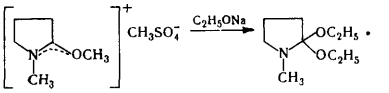
Another method for the synthesis of lactam acetals consists in the interaction of *N*-substituted lactams with phosgene, resulting in the formation of the corresponding amide-chlorides, from which the acetals are obtained by treatment with sodium ethoxide or triethylamine in alcohol[50,132]:



It has been stated that this reaction takes place by the following hypothetical mechanism[132]:

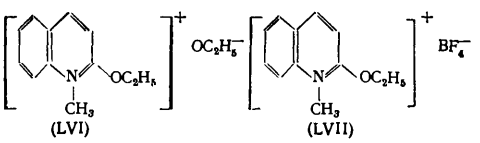


The preparation of lactam acetals by the interaction of the complex of *N*-methyl-2-pyrrolidone and dimethyl sulphate with sodium ethoxide, similar to the procedure where lactim ethers are obtained by treating lactams with triethyloxonium fluoroborate or dimethyl sulphate, has been also described[129]:



The chemical properties of lactam acetals have been inadequately investigated, although there is an indication[130] that these compounds are similar in their chemical behaviour to the acetals of non-cyclic acid amides, which have been investigated in greater detail[130,134,135]. Like lactim ethers, lactam acetals enter fairly readily into nucleophilic substitution reactions. In particular, on reaction with water, these compounds are hydrolysed relatively easily with formation of the corresponding lactams.

In this connection the comparative reactivities of the acetals of *N*-methyl-2-quinolone (LIII), *N*-methyl-2-benzothiazolone (LIV), and *N*-methyl-2-benzoxazolone (LV) should be mentioned[130]. It has been established that compound (LIII) hydrolyses so readily that it is difficult to isolate it in a pure form. In contrast to compound (LIII), compounds (LIV) and (LV) are relatively stable to hydrolysis. In order to account for this phenomenon, it has been suggested that the acetal (LIII) exists partially in the ionised form (LVI):

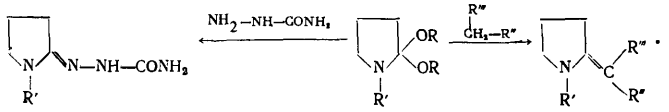


(LVI) (LVII)

The formation of compound (LVI) is facilitated in this case by the complete aromatisation of the quinoline ring and the presence of the above ionised species leads of course to an enhanced reactivity in relation to nucleophilic reagents [compared with compounds (LIV) and (LV)]. This hypothesis was confirmed by the relatively high electrical conductance of solutions of compound (LIII) in nitrobenzene and dimethylformamide and also by the fact that the fluoroborate complex (LVII) is much more stable to hydrolysis than the corresponding complex obtained from *N*-methyl-2-benzoxazolone and *N*-methyl-2-benzothiazolone. Similar relative reactivities of compounds (LIII), (LIV), and (LV) are observed also in other nucleophilic substitution reactions.

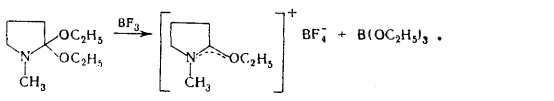
Among the reactions of lactam acetals with nucleophilic reagents, the interaction of the acetals of *N*-methyl-2-pyrrolidone with semicarbazide, with formation of the corresponding semicarbazone, as well as reactions with

compounds having active methyl or methylene groups have also been reported[130]:

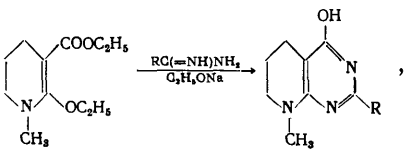


It is noteworthy that the last reaction takes place as a rule extremely readily, which suggests that the acetals are more reactive than lactim ethers.

The high reactivity of the acetals is also shown in the reaction of the diethylacetal of *N*-methyl-2-pyrrolidone with boron trifluoride accompanied by the elimination of one alkoxy-residue and the formation of the fluoroborate complex (LII)[131]:



In conclusion we may quote the condensation of 3-ethoxycarbonyl-2-ethoxy-*N*-methyltetrahydropyridine with guanidine and thiourea, resulting in the formation of 2-substituted 4-hydroxy-8-methyl-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidines[133]:



where R = NH_2 or SH.

This reaction shows that the conversion of lactim ethers to *O*-alkyl derivatives of lactams with a substituent at the ring nitrogen atom gives rise to the possibility of the synthesis of condensed heterocyclic compounds with predetermined positions of the substituents.

The use of *O*-alkyl derivatives of lactams in organic synthesis has led to important results both as regards synthesis and theory. A large number of heterocyclic compounds, in particular examples of new heterocyclic systems which are of interest both biologically and chemically, have been synthesised on their basis. The wide choice of reagents and their relative availability combined with high reactivity give rise to a wide range of applications of *O*-alkyl derivatives of lactams as starting materials in the synthesis of a wide variety of organic compounds.

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Ordzhonikidze All-union Institute of
Chemistry and Pharmacology,
Moscow

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The Chemistry of Corrin Systems

T.A.Melent'eva, N.D.Pekel', and V.M.Berezovskii

The review deals with the modern state of the chemistry of corrin compounds. The principal methods of the synthesis of corroles, metal complexes of tetradehydrocorrins and corrins are discussed together with the mechanisms of the cyclisation of tetrapyrrole systems on irradiation or in the presence of metal salts, which leads either to corroles or tetradehydrocorrin complexes. The limits of the applicability of the methods for the synthesis of corrins via imino-ethers and by the reduction of tetradehydrocorrins are estimated. The results of studies on the stereospecific synthesis of cobyrinic acid are presented. The available literature data on the properties of synthetic corrinoid systems are considered as well as the properties of the metal complexes, deuterium exchange, protonation and alkylation of corroles and corrins and the rearrangements of tetradehydrocorrins. Much attention has been devoted to the spectroscopic characteristics of tetrapyrrole macrocyclic compounds, in particular their ultraviolet, infrared, and NMR spectra, which are widely used to establish the structure of corrin systems. The bibliography includes 82 references.

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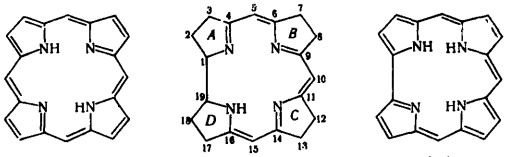
I. INTRODUCTION

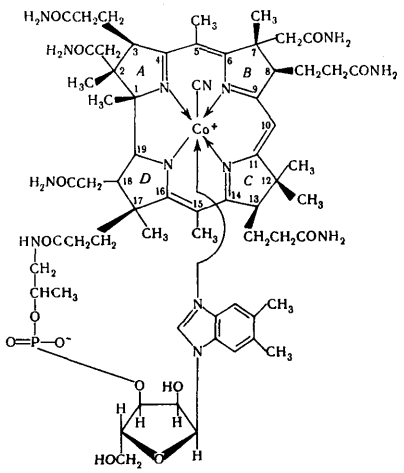
The attention of chemists is at present increasingly drawn to biologically active substances which play an important role in the living processes of organisms. Such substances are in particular the macrocyclic tetrapyrrole systems, two types of which are encountered in nature. The first type consists of porphyrins (I), for example haemin, which is the basis of the blood pigment (haemoglobin) and cytochrome coenzymes, and also dihydroporphyrins or chlorins, for example the pigment in plant leaves—chlorophyll. The second type consists of corrins (II)†, for example cobalamins, represented by vitamin B_{12} and its coenzyme:



(I) (II) (IV)

Both types include important natural compounds, characterised by a similar asymmetric distribution of β-substituents in the ring and the fact that they exist as metal complexes. The close relation between these two groups is demonstrated by the fact that the early stage of their biosyntheses includes porphobilinogen[2-4].

Vitamin B_{12} (cyanocobalamin) (III) counteracts pernicious anemia. As a coenzyme, vitamin B_{12} catalyses many enzymic reactions, in particular the conversion of glutamate into methylaspartate[5], succinyl-coenzyme A into methylmalonyl-coenzyme A,[6,7] and 1,2-diols into deoxyaldehydes[8-11] and the dissociation of lysine into aliphatic acids and ammonia[12]. The methyl analogue of the vitamin B_{12} coenzyme takes part in the synthesis of methionine[13] and the cobamide coenzyme serves also as a cofactor in the reduction of ribonucleosides[14] and in the synthesis of egg albumin[15].



(III)

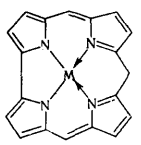
The chemical structure of vitamin B_{12} has been completely elucidated as a result of a brilliant application of X-ray diffraction analysis[16] and studies on chemical degradation[2]. The cobalamine molecule can be divided into two parts, known as the "planar" part and the "nucleotide"; the latter lies in a plane almost perpendicular to the planar component. In the planar part the central cobalt atom is linked to four reduced pyrrole rings, forming a macrocycle. Three of the four junctions are formed by the *meso*-carbon atoms and in the fourth position the junction is formed by a direct bond between two α-carbon atoms of the heterocyclic rings. The macrocycle contains six conjugated double bonds and nine asymmetric carbon atoms.

† The name "corrin" is given to the macrocyclic compound (II) which constitutes the basis of vitamin B_{12}; it was adopted in 1957 at the First International Symposium on Vitamin B_{12}.[1]

Several reviews have been written on the chemistry and biochemistry of vitamin B_{12} and its coenzyme[2,17-20].

The macrocyclic compound (IV), differing from corrin by four additional double bonds and constituting an 18π-electron aromatic system, was synthesised[21] in 1964. This compound was called "corrole"[22]. It is of independent interest as a new aromatic heterocyclic system.

At present three types of new heterocyclic compounds[23] with two directly linked pyrrole rings and containing ten double bonds are known: corroles (IV) and their metal complexes (V), neutral nickel and cobalt complexes of 1-substituted tetradehydrocorrins (VI) and salts of the nickel and cobalt complexes of 1,19-disubstituted tetradehydrocorrins (VII). The last two macrocyclic compounds are not aromatic, and therefore they are referred to as tetradehydrocorrins and not substituted corroles.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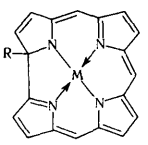
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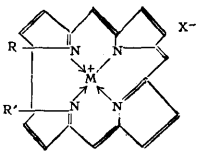

(VII)

The structure of tetradehydrocorrins includes, like that of corroles, a direct α-carbon–α-carbon bond between two pyrrole rings but differs from corrins by a higher degree of unsaturation. Possibly pyrroles and tetradehydrocorrins are intermediates in the biosynthesis of vitamin B_{12}. In the study of the biosynthesis of cobalamin[3,24] it was established that porphobilinogen is a precursor of both corrin and porphyrins. It is believed[20,25-27] that porphobilinogen condenses to a linear tetrapyrrole system and the latter cyclises either into porphyrin or into corrin, possibly via corrole.

The complete chemical synthesis of vitamin B_{12} has not as yet been achieved. The most difficult problem is the stereospecific synthesis of the central heterocyclic part of the molecule with the required substituents.

II. METHODS FOR THE SYNTHESIS OF CORRIN SYSTEMS

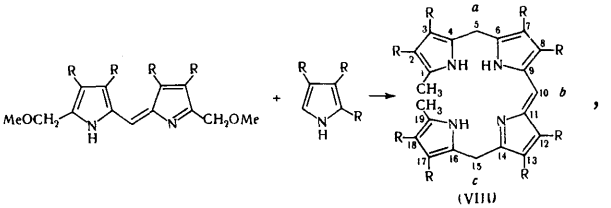
A. SYNTHESIS OF CORROLES AND TETRADEHYDROCORRINS

1. Synthesis of Corroles by Photocyclisation

Methods for the synthesis of corrole and tetradehydrocorrins were developed by Johnson and coworkers. Corroles are synthesised by the photocyclisation of linear tetrapyrrole systems, namely the dihydrobromides of 1,19-dideoxybiladienes-*ac*[28-31] and the hydrobromides of 1,19-dideoxybilenes *b*‡[28,32]. Special methods have been developed for the preparation of these tetrapyrrole systems.

‡ Since the bile pigments (bilirubin) are the most thoroughly investigated tetrapyrrole systems, the bile pigment nomenclature has been adopted for all the tetrapyrrole systems[33]. The prefix "deoxy" indicates the absence of two hydroxy-groups in positions 1 and 19.

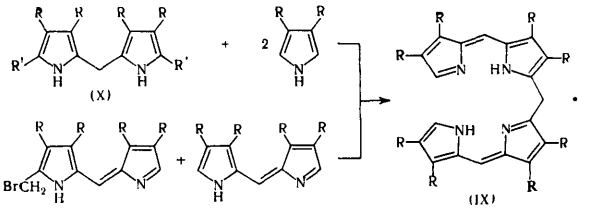
Bilenes-*b* (VIII) were synthesised by the condensation[28,32] of 5,5′-di(methoxymethyl)dipyrromethene with two equivalents of 2,3,4-trialkylpyrrole:


(VIII)

where R = H, CH_3, or C_2H_5.

Two methods have been developed for the synthesis of biladienes-*ac* (IX).

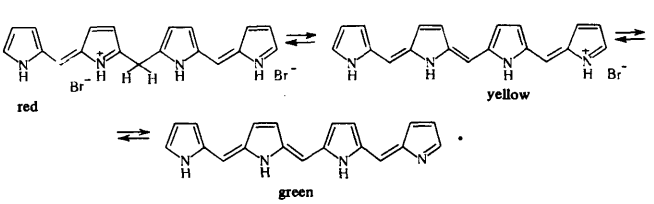
1. Condensation[28] of 5,5′-diformyldipyrromethane (X, R′ = CHO) with two equivalents of 3,4-dialkylpyrroles or condensation of dipyrromethane-5,5′-dicarboxylic acids (X, R′ = COOH) with two equivalents of 5-formyl- or 5-acetyl-pyrroles:


(X) (IX)

2. Condensation[29-31] of 5-bromomethyldipyrromethene with dipyrromethene having a free α-position in the presence of tin chloride.

Corrole was obtained for the first time[34] by irradiating with the light from a tungsten lamp a suspension of a biladiene-*ac* in boiling methanol in the presence of a base. This results in the formation of a solution, the colour of which rapidly changes from yellow to green and then to red; from the last solution, crystals of corrole (IV) precipitate on cooling[35]. Relatively stable nickel and copper complexes of corrole[35], which may be obtained by the addition of metal cations either to solutions of corroles or to a suspension of 1,19-dideoxybiladienes-*ac* before irradiation, have been isolated.

The exact mechanism of the photocyclisation of biladienes-*ac* to corroles has still not been established[36,37], but it is most probable that the reaction has a free-radical mechanism[23,37]. Protons in the 10-position are definitely involved in the cyclisation. Solutions of the dihydrobromides of 1,19-dideoxybiladienes in benzene are red, while those in alcohol and in dimethyl sulphoxide are yellow, becoming green on addition of a base, for example piperidine. The colour change is caused by the abstraction of a proton in the 10-position by polar solvents and the formation of the monohydrobromide of 1,19-dideoxybilatriene-*abc*, which is converted into a free base under the action of piperidine.

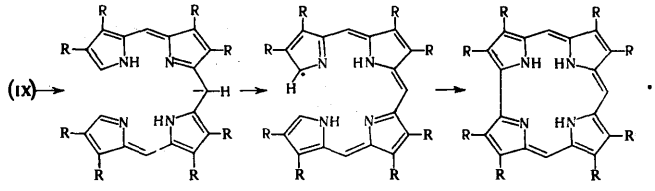

red yellow green

Photocyclisation of biladienes-*ac* is possible only in the presence of bases, which indicates the initial elimination of a proton from the central methylene group during the

photocyclisation process. This hypothesis is confirmed by the fact that 10,10-dimethylbiladienes are not cyclised to corroles[32].

Apart from the protons at the C_{10} atom, the photocyclisation is greatly affected by substituents in the 1- and 19-positions and also by the presence of metals. Corrole could not be obtained from 1,19-dimethylbiladiene by photocyclisation, while the cyclisation of biladienes unsubstituted in the 1- and 19-positions takes place readily. The reason for this is that the 1,19-dimethyl or 1,19-diethoxycarbonyl groups give rise to steric hindrance to cyclisation.

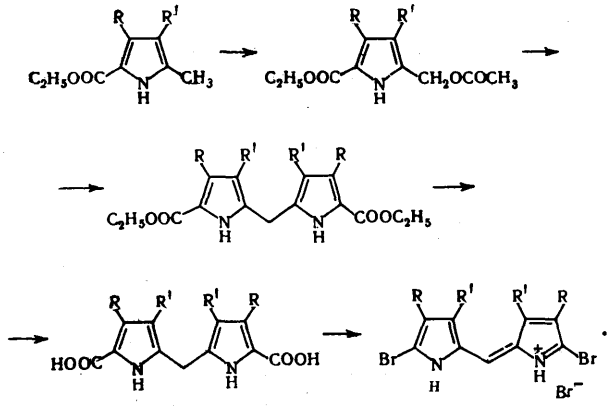
The mechanism proposed for the formation of corrole includes the formation of an intermediate radical:



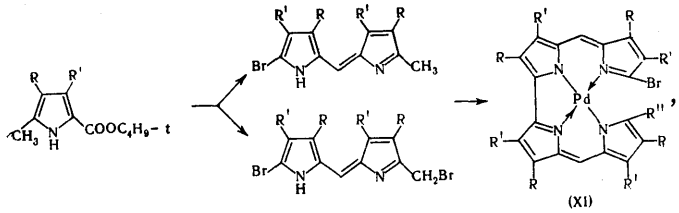
The effect of various free-radical initiators and one-electron oxidising agents on the cyclisation of 1,19-dideoxy-2,3,7,8,12,13,17,18-octa-alkylbiladienes-*ac* in the presence of ammonia has been examined[37]. When potassium hexacyanoferrate(III), ferric chloride, ceric sulphate, hydrogen peroxide, benzoyl peroxide, or t-butyl peroxide are added, cyclisation takes place readily and the replacement of atmospheric oxygen by nitrogen does not affect the rate of reaction and the yield of corroles; the corroles are formed in yields of 68–84%.

2. Attempts at Synthesis of Corrole by the Introduction from the Outside of a *meso*-Carbon Atom and Cyclisation of Tetrapyrrole Systems on Introduction of Hetero-Atoms

The cyclisation of various tetrapyrrole systems with introduction from the outside of a *meso*-carbon atom has been investigated as one of the possible ways of synthesising corrole[21,32,38]. The initial dipyrromethenes with symmetrical β-substituents were synthesised from substituted 5-ethoxycarbonyl-2-methylpyrroles[39], which, on oxidation with lead tetra-acetate, are converted into 2-acetoxymethylpyrroles and in an acid medium the latter are condensed into dipyrromethanes. After the hydrolysis of the ester groups, dipyrromethane-5,5′-dicarboxylic acid is treated with bromine in acetic acid and the hydrobromide of β-substituted 5,5′-dibromodipyrromethene is obtained[40]:



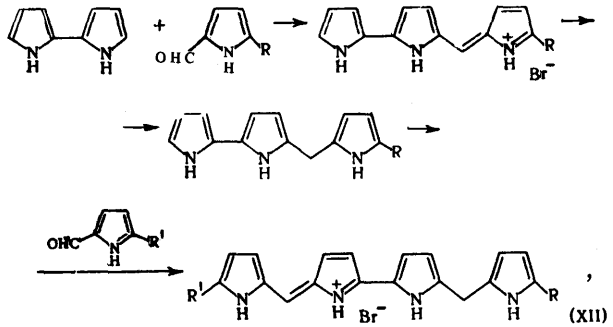
Dipyrromethenes with asymmetric β-substituents can be obtained by the action of bromine on the t-butyl ester of 5-methylpyrrole-2-carboxylic acid[41]; this results in the formation of a mixture of 5-bromo-5′-methyldipyrromethene and 5-bromo-5′-bromomethyldipyrromethene. The condensation of these pyrromethenes in the presence of palladium on strontium carbonate yields the chelate complex (XI, R″ = CH_3), which could not be cyclised. When two moles of 5,5′-dibromodipyrromethene were condensed in the presence of palladium on strontium carbonate or in the presence of copper and cobalt salts[22], the corresponding metal complexes (XI, R″ = Br) were obtained but these could not be cyclised either under the action of formaldehyde in an acid medium:



(XI)

where R = R′ = H, R = R′ = CH_3, or R = CH_3 and R′ = Br.

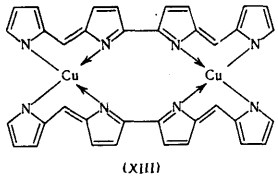
Tetrapyrrole systems (XII) containing a direct α-carbon–α-carbon bond between the two pyrrole rings have been used to synthesise corroles[38]. Two methods have been proposed for the preparation of compound (XII). When 2,2′-bipyrroles are condensed[28,42] with 2-formylpyrrole[43], one molecule of formylpyrrole adds on and 5-(pyrrol-2-yl)dipyrromethene is formed; hydrogenation of the latter yields pyrrolyldipyrromethane, the reaction of which with 2-formylpyrrole gives compound (XII):



(XII)

where R = R′ = H, R = R′ = CH_3, or R = CH_3 and R′ = Br.

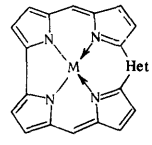
The second method of synthesising compound (XII) consists in the condensation[32] of 2-chloromethylpyrroles with 5-(pyrrol-2-yl)dipyrromethenes in the presence of tin chloride. In the cyclisation of the tetrapyrrole system (XII) in the presence of copper[32] or zinc[44] acetates, the corresponding chelate complexes of type (XI) and the copper complex (XIII) where isolated.



(XIII)

However, it it was not possible to introduce the *meso*-carbon atom into the tetrapyrrole system and cyclise the latter into corrole, a pseudocorrole system could be synthesised by the external introduction of a hetero-atom (O, N, or S).

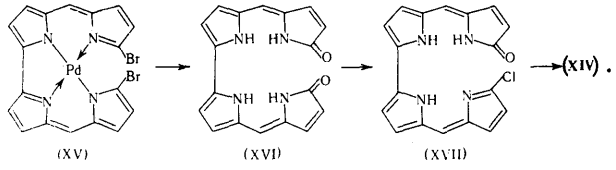
Oxa-, aza-, methylaza-, and thia-analogues of corrole (XIV) are planar compounds; each of the bridge atoms (Het = O, N, or S) contains at least one pair of free electrons which participate in the overall conjugated macrocyclic system:



(XIV)

In the condensation of two molecules of 5-bromodipyrromethenes in the presence of palladium on strontium carbonate a tetrapyrrole palladium complex (XV) [22] was obtained; when refluxed in the presence of hydrochloric acid it yielded a cyclic product to which the structure of a hydroxopalladium complex of corrole was initially ascribed [22]. Subsequent studies [45,46] showed that this compound is a derivative of the cyclic ether (XIV) (Het = O) in which the C_{10} carbon atom has been replaced by oxygen. Nickel and copper complexes of this ether have been synthesised.

The mechanism of the cyclisation of the free tetrapyrrole dibromide to the cyclic ether is probably as follows: in the course of the acid hydrolysis of the dibromide two products are formed—a dilactam (XVI) and a monolactam (XVII); the latter is produced as a result of the hydrolysis of one bromine atom and replacement of the second bromine atom by chlorine. Under the action of copper(II) acetate, nickel chloride, and palladium(II) chloride, the monolactam (XVII) is converted into complexes of the cyclic ether (XIV):



(XV) (XVI) (XVII)

Possibly the monolactam (XVII) isomerises initially to a lactim form, which in fact gives rise to the metal complexes.

The macrocyclic ether (XIV Het = O) can be obtained in a free form when copper is removed by treating the copper complex with concentrated sulphuric acid at 20°C. When the copper complex is treated with hot concentrated hydrochloric acid, the ring opens with formation of the monolactam (XVII). Under these conditions, nickel and palladium complexes are not converted into the dilactam (XVI), i.e. ring opening is facilitated by preliminary removal of the metal.

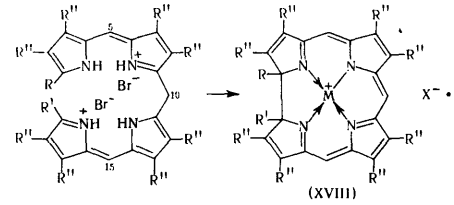
Treatment of the free cyclic ether with metal salts results in the formation of the corresponding metal complexes. The attempts to synthesise the macrocyclic ether (XIV) from the dibromides of the nickel and cobalt chelate complexes of type (XV) resulted in the formation of the dilactam (XVI) only.

The aza- and thia-derivatives (XIV, Het = NH, NCH_3, S) were synthesised by treating the palladium derivative (XV) in pyridine with ammonia, methylamine, or sodium sulphide respectively. The cyclic aza-derivatives were obtained in the form of both palladium and copper complexes as well as the free cyclic compounds.

3. Synthesis of Metal Complexes of Tetradehydrocorrins

Since in natural corrins the macro-ring has an angular 1-methyl group, the synthesis of various tetrahydrocorrins with angular substituents attracted much attention.

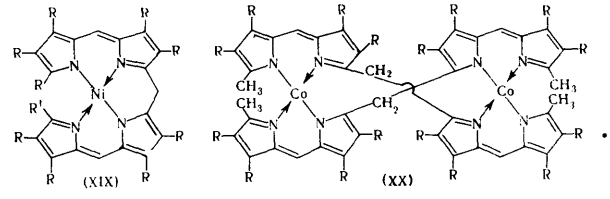
Aeration [47] of solutions of dihydrobromides of 1,19-dimethyl- or 1,19-diethoxycarbonyl-1,19-dideoxybiladienes-*ac* in the presence of bases and nickel or cobalt acetates yields salts of the nickel or cobalt complexes of 1,19-substituted tetradehydrocorrins (XVIII, M = Ni or Co, and R = R′ = CH_3 or $COOC_2H_5$): [48,49]



(XVIII)

Treatment of the methanol solutions of the dihydrobromides of 1,19-dimethyl-1,19-dideoxybiladienes-*ac* or the corresponding bilenes-*b* with copper salts results in the formation of porphyrin, the cyclisation of which takes place with the loss of one carbon atom [33].

When methanol solutions of 1,19-dimethyl-1,19-dideoxybiladiene-*ac* are heated with sodium and nickel acetates, a chelate nickel complex of biladiene (XIX) is formed initially and on further aeration and treatment with NO_3^-, Cl^-, or ClO_4^- ions cyclises into a complex of 1,19-dimethyltetradehydrocorrin (XVIII). In the reaction of 1,19-dimethyl-1,19-dideoxybiladienes-*ac* with cobalt acetate, the biladiene cobalt complex was not isolated; in this case the formation of the cobalt complex of 1,19-dimethyltetradehydrocorrin is accompanied by that of compound (XX), containing two tetrahedral cobalt atoms and two biladiene ligands [47]. Under the conditions of mass-spectrometric analysis, this dimer dissociates and cyclises with the elimination of hydrogen, being converted into the cobalt complex of 1,19-dimethyltetradehydrocorrin. The cyclisation of 1,19-disubstituted 1,19-dideoxybiladienes can be achieved only in the presence of a metal:

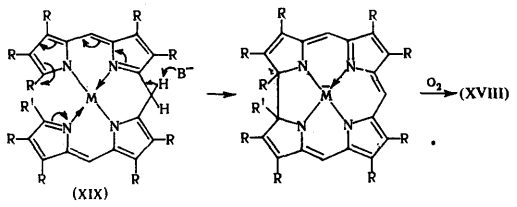


(XIX) (XX)

For a more detailed investigation of the cyclisation of biladienes, certain biladienes with substituents in the 5-, 10-, and 15-positions were synthesised [47]. It was found that the cyclisation of 10,10-dimethylbiladienes is impossible under any conditions. The cyclisation products of 5,10-dimethylbiladienes were not identified. The cyclisation of 5,15-dimethyl- and 10-methyl-biladienes yielded the salts of the nickel complexes of 5,15-dimethyl-10-methyl-tetradehydrocorrins, the cyclisation of 10-methylbiladienes being much slower than that of biladienes with a free 10-position.

The following mechanism was proposed for the cyclisation of 1,19-disubstituted 1,19-dideoxybiladienes-*ac* on the basis of these observations [36,47]. Initially a metal complex (XIX) is formed, the metal having a coordinating effect on the 1- and 19-positions, bringing them closer together and thereby facilitating the cyclisation. In the presence of

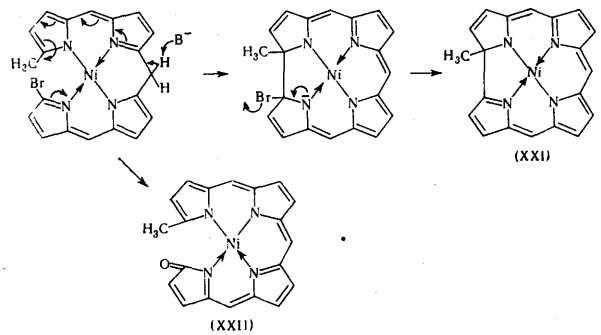
a base, the proton is eliminated from the C_{10} atom and an anion is formed, which on oxidation with atmospheric oxygen is converted into a complex of 1,19-disubstituted tetradehydrocorrin (XVIII):



(XIX) (XVIII)

To synthesise tetradehydrocorrins with an angular 1-methyl group, the dihydrobromides of 19-bromo-1-methyl-1,19-dideoxybiladienes-*ac* were cyclised. When methanol solutions of these compounds are heated with bases in the presence of nickel ions[50], nickel complexes of 1-methyltetradehydrocorrin (XXI) are readily formed in the absence of atmospheric oxygen[51]. The presence of air causes the formation of the nickel complex of the lactam (XXII); ordinary heat treatment of 19-bromo-1-methyl-1,19-dideoxybiladienes results in the formation of porphyrins[51].

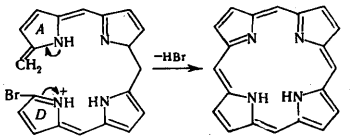
The mechanism of the formation of 1-methyltetrahydrocorrins can be represented as follows:



(XXI) (XXII)

In contrast to cyclisation which leads to complexes of 1,19-disubstituted tetradehydrocorrins, the formation of 1-methyltetradehydrocorrins includes the elimination of hydrogen bromide without an oxidation stage. The cyclisation is very rapid and the nickel complex of the biladiene was not isolated. In contrast to the alkaline cyclisation of 19-bromo-1-methyl-1,19-dideoxybiladienes, the formation of porphyrins[30,52] includes a stage involving the formation of an intermediate with an enamine structure of ring *A* followed by the attack of the enamine on the α-carbon atom of ring *D*.

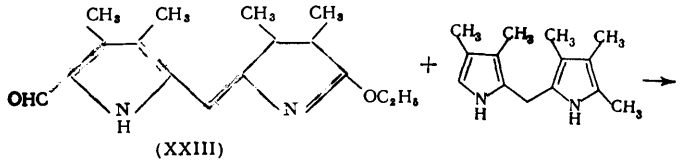
The cyclisation of 19-bromo-1-methyl-1,19-dideoxybiladienes was extended to 1-ethyl and 1-isopropyl-1,19-dideoxybiladienes, which were converted into the nickel complexes of the corresponding 1-alkyltetradehydrocorrins.



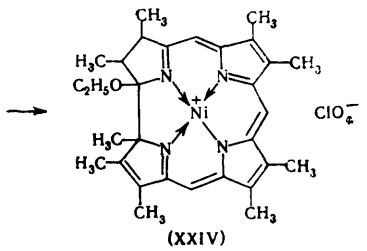
Attempts were made to activate the cyclisation of 19-bromo-1-methyl-1,19-dideoxybiladienes using copper acetate instead of nickel acetate, but the sole reaction product was then the copper complex of porphyrin. The cyclisation of 19-bromo-1-methyl-1,19-dideoxybiladienes in the presence of cobalt acetate in various solvents yielded a mixture of products. These results are inconsistent with the ease of isolation of the cobalt complexes of 1,19-disubstituted tetradehydrocorrins[47] and can be accounted for by the high reactivity of the cobalt complex of 1-methyltetradehydrocorrin. Hydrogenation of solutions obtained after treating 19-bromo-1-methyl-1,19-dideoxybiladienes with cobalt acetate over Raney nickel at 100°C under a pressure of 100 atm yields the cobalt complex of 1-methylcorrin[23].

The cyclisation of biladienes[53] containing the 19-alkoxy- instead of the 19-bromo-group has been described, but the use of such compounds proved to be less convenient. The cyclisation of the dihydrobromides of 19-ethoxycarbonyl-1-methyl-1,19-dideoxybiladienes-*ac*[47] yields the nickel complexes of 19-ethoxycarbonyl-1-methyltetradehydrocorrins; the ester group may be removed by hydrolysis followed by decarboxylation.

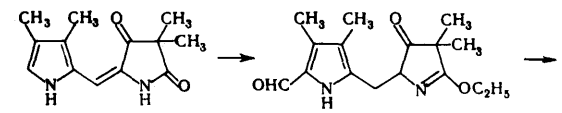
The cyclisation of certain reduced pyrrole derivatives constitutes a modification of the biladiene synthesis[53]. Condensation of the imino-ether (XXIII), obtained by the action of the Meerwein reagent[54,55] on the corresponding pyrrolidone, with 5-methyldipyrromethane yields a linear tetrapyrrole derivative, which is cyclised, without isolation, by aeration in the presence of nickel acetate into the complex (XXIV) containing 9 double bonds. The condensation of 3,3-dimethylpyrrole-2,4-dione with 2-formyl-3,4-dimethylpyrrole yields the dipyrromethene (XXV), which is hydrogenated, formylated, and converted into an imino-ether. The condensation of the latter with 5-ethoxycarbonyl-3,3′,4,4′-tetramethyldipyrromethane in the presence of nickel acetate yields the complex (XXVI) containing 8 double bonds:



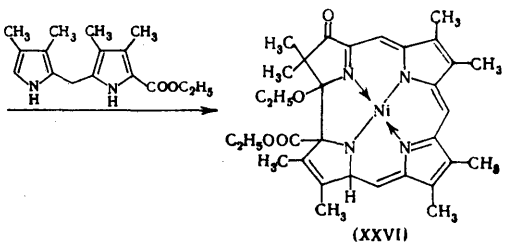
(XXIII)



(XXIV)



(XXV)



(XXVI)

B. SYNTHESIS OF CORRINS

There exist three approaches to the synthesis of the corrin ring—the central component of vitamin B_{12}. On the basis of the biosynthetic mechanism of the formation of corrin, Johnson[23] carried out the ring-closure of linear tetrapyrrole systems with subsequent reduction of the resulting macrocyclic compounds—metal complexes of tetrehydrocorrins.

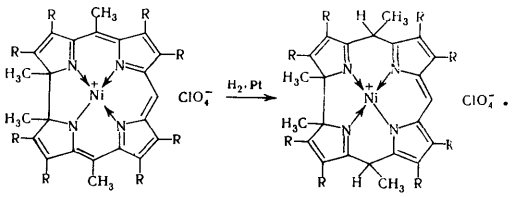
Eschenmoser and coworkers[56] achieved the synthesis of corrin from compounds oxidised to the same extent as the natural corrin compounds, using imino-ethers as the electrophilic components in the condensation reaction involving the formation of C–C bonds.

Neither of these methods permits the synthesis of corrins with a definite steric disposition of the β-substituents, analogous to their disposition in the corrin ring of vitamin B_{12}, where there are nine asymmetric centres. Woodward[57] is close to achieving the stereospecific synthesis of the corrin ring.

1. Synthesis of Corrins and Mono- and Di-dehydrocorrins by the Reduction of Tetradehydrocorrins

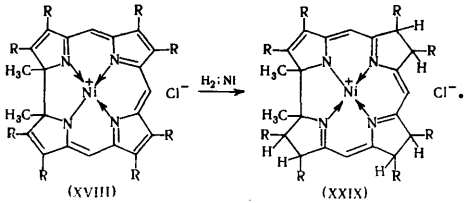
One of the methods for the synthesis of corrins is reduction of 1-methyltetradehydrocorrins. In the course of studies on the conditions governing the formation of corrins, a number of macrocyclic compounds intermediate between corrins and tetradehydrocorrins as regards degree of oxidation have been synthesised.

In the hydrogenation of corrole solutions[35] in the presence of platinum an extremely unstable unidentified product was isolated, which was rapidly oxidised in air and converted into the initial corrole. In the hydrogenation of the nickel complex of 1,5,15,19-tetramethyltetradehydrocorrin (XXVII)[47] in the presence of platinum the compound combines with one mole of the hydrogen and an amorphous very unstable orange perchlorate is formed, the ultraviolet spectrum of which resembles that of the nickel complex of dipyrromethene; the possible structure of the hydrogenated compound is represented by formula (XXVIII).



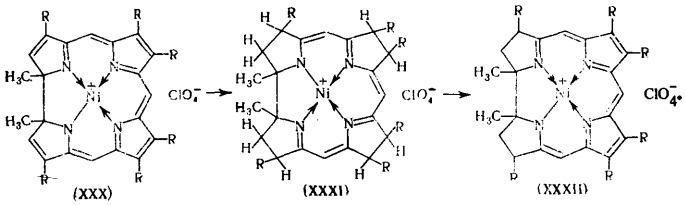
(XXVII) (XXVIII)

The salts of the nickel and cobalt complexes of 1,19-dimethyltetradehydrocorrins could not be reduced with zinc in acetic acid or sodium borohydride in methanol nor could they be hydrogenated over platinum[47]. The hydrogenation of the chloride and perchlorate of the nickel complex of 1,19-dimethyltetradehydrocorrin (XVIII) in the presence of Raney nickel at 100°C and a pressure of 100 atm proved to be more successful. Under these conditions, the product is the orange-yellow salt of the nickel complex of monodehydrocorrin (XXIX) containing seven double bonds. It is stable to oxidation and does not break down under the action of acids and alkalis:



(XVIII) (XXIX)

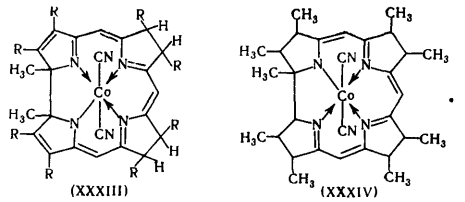
In all the corrins known at the present time[56] the directly linked pyrrole rings do not contain a ββ-double bond. Since the ββ-double bond of ring *A* in compound (XXIX) is sterically protected, a study was made of the hydrogenation of the perchlorate of the nickel complex of 1,19-dimethyltetradehydrocorrin (XXX) with free 2- and 18-positions[23], which results in the formation of the salt of the nickel complex of 1,19-dimethylcorrin (XXXI):



(XXX) (XXXI) (XXXII)

When compound (XXXI) is heated with alcoholic potassium hydroxide in air, a purple substance is rapidly formed, the ultraviolet and visible spectra of which are analogous to those of the tetradehydrocorrin complex but with an overall hypsochromic shift; the NMR spectrum corresponds to 7,12-didehydrocorrin (XXXII).[58] Similar dehydrogenation by bases in the presence of oxygen was observed previously[59].

The hydrogenation of the perchlorate of the cobalt complex of 1,19-dimethyltetradehydrocorrin (XVIII)[47] in the presence of Raney nickel at 100°C and a pressure of 100 atm leads to didehydrocorrin (XXXIII) after treatment with sodium cyanide, while hydrogenation of the cobalt complex of 1-methyltetradehydrocorrin of type (XXI)[23] under the same conditions gives 1-methylcorrin (XXXIV), isolated in the form of the cyanide. It is an amorphous product (probably a mixture of stereoisomers), its visible spectrum coincides with that of dicyanocobalamin, and the NMR spectrum indicates the presence of three *meso*-protons and the absence of olefinic substituents:



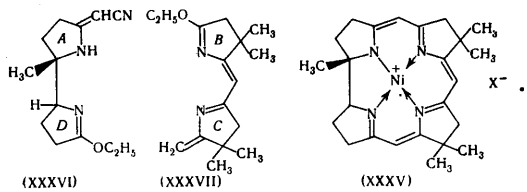
(XXXIII) (XXXIV)

Partial hydrogenation of substituted corrins and tetradehydrocorrins gives rise to asymmetric carbon atoms and the reaction products are mixtures of stereoisomers. Thus the reduction of tetradehydrocorrins cannot be used as a method for synthesising corrin systems analogous to natural corrins and by this method one cannot obtain compounds with a specified steric disposition of β-substituents.

2. Synthesis of Corrins via Imino-ethers

Corrins containing certain β-methyl substituents were synthesised for the first time by Eschenmoser and coworkers in 1964.[56] Imino-ethers[60] were used in this synthesis as the electrophilic components of the condensation in the formation of the nitrogen–carbon conjugated chain of the corrin chromophore[61,62]. These reactions were possible owing to the Meerwein reagent—triethyloxonium tetrafluoroborate[55].

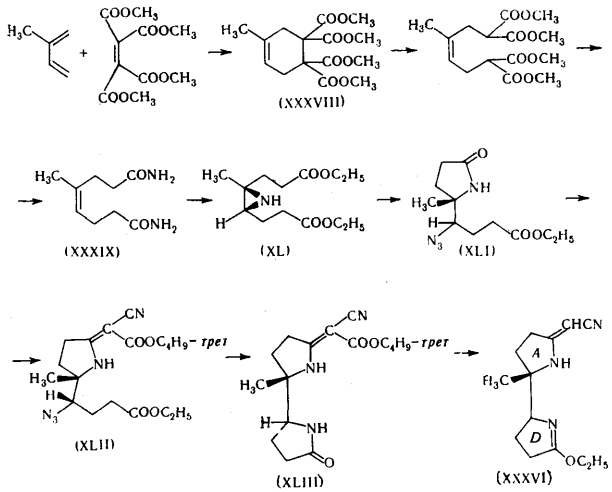
The synthesis of the corrin macrocyle (XXXV) consists of three principal stages: the formation of the *A*–*D* ring system (XXXVI), the formation of the *B*–*C* ring system (XXXVII), and finally the condensation of both systems with closure of the macroring (XXXV):[62]



(XXXVI) (XXXVII) (XXXV)

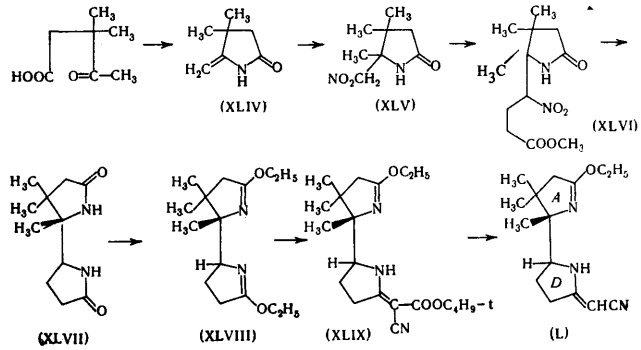
In the synthesis of the *A*–*D* ring system (XXXVI) the starting material is the tetraester (XXXVIII), which is obtained by the Diels–Alder reaction (see Scheme I).

Scheme 1



(XXXVIII) (XXXIX) (XL) (XLI) (XLII) (XLIII) (XXXVI)

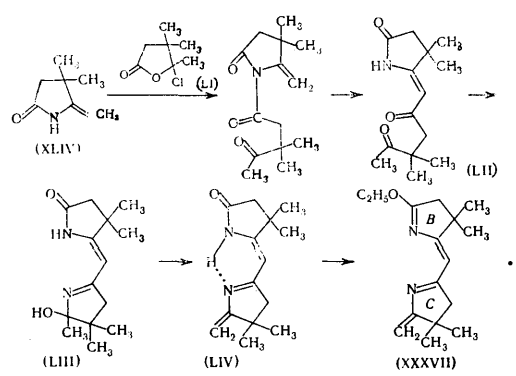
The opening of the ring (XXXVIII) leads to an aliphatic tetraester, which is converted under the action of sodium in liquid ammonia into the crystalline diamide (XXXIX). Stereospecific imination of the double bond in compound (XXXIX) followed by hydrolysis yields an aziridine derivative with the *cis*-configuration (XL). Under the action of the azide ion, a second nitrogen atom is introduced into the molecule with the opening of the aziridine ring and the formation of the butyrolactam ring (XLI). Condensation of the latter with butyl cyanoacetate leads to the ester (XLII). Selective catalytic hydrogenation of the azido-group in compound (XLII) results in the formation of the bicyclic monolactam (XLIII). Elimination of the butyl ester group by treatment with anhydrous trifluoroacetic acid and alkylation of the lactam group with an excess of triethyloxonium tetrafluoroborate yields the *A*–*D* ring system (XXXVI).



(XLIV) (XLV) (XLVI) (XLVII) (XLVIII) (XLIX) (L)

The cyclic enamide (XLIV) was used as the starting material in the synthesis of the *A*–*D* ring system. On nucleophilic addition of nitroethane to compound (XLIV) in the presence of potassium t-butoxide, the nitro-derivative (XLV) is formed. The Michael condensation of methyl acrylate with compound (XLV) yields a mixture of diastereoisomers (XLVI) which on reduction in the presence of Raney nickel is converted into a mixture of the diastereoisomeric dilactams (XLVII); the latter are readily separated by virtue of their different solubilities. The dilactam (XLVII) is converted[54,61] into the di-imino-ether (XLVIII), the treatment of which with butyl cyanoacetate gives compound (XLIX); the conversion of only one imino-group in compound (XLIX) is due to steric factors; compound (XLIX) is converted into compound (L).

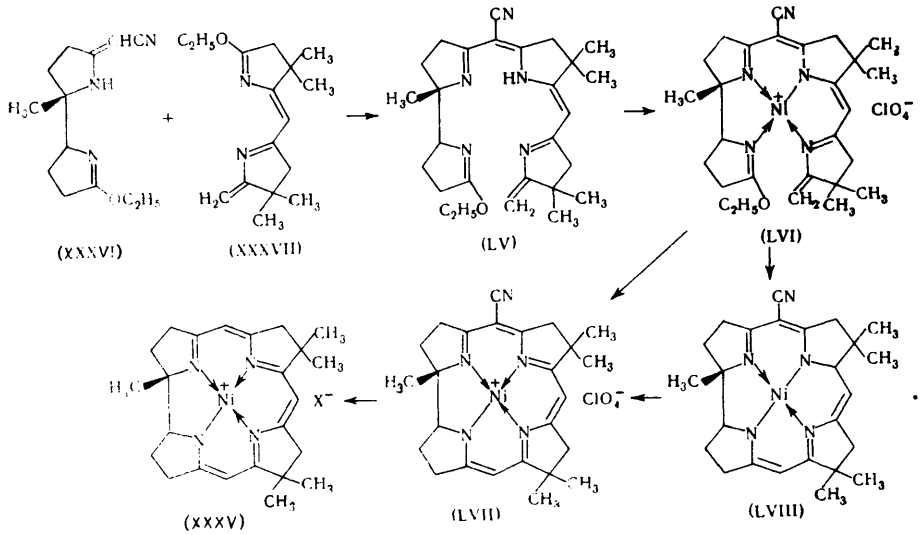
In the synthesis of the *B*–*C* ring system the starting material was also compound (XLIV). *N*-Acylation of the potassium salt of this enamide with a pseudo-acid chloride (LI) followed by photochemical rearrangement leads to compound (LII). The replacement of the carbonyl oxygen atom in compound (LII) by a nitrogen atom is achieved by the action of ammonia in methanol, which results in compound (LIII), the tertiary hydroxy-group of which is readily eliminated with formation of compound (LIV). Because of the intermolecular hydrogen bond in compound (LIV), when the latter is acted upon by triethyloxonium tetrafluoroborate, only *O*-alkylation takes place with formation of compound (XXXVII):



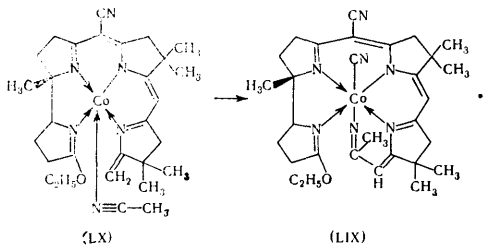
(XLIV) (LI) (LII) (LIII) (LIV) (XXXVII)

The main synthetic problem is the combination of both corrin components: the *A*–*D* (XXXVI) and *B*–*C* (XXXVII) ring systems[56]. It was solved using the specific C → C condensation of the β-iminocrotononitrile group of compound (XXXVI) with the imino-ether group of compound

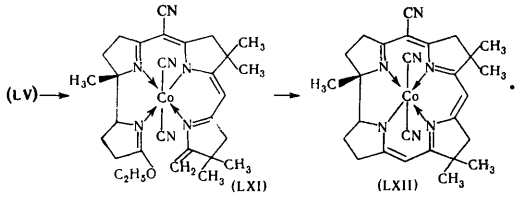
(XXXVII), leading to compound (LV), isolated as the sodium salt. The interaction of this salt with nickel perchlorate in acetonitrile yields the planar complex (LVI), where the imino-ether group and the exocyclic methylene group are sterically fixed, i.e. the geometrical conditions for the closure of the macroring have been created. When compound (LVI) is acted upon by potassium t-butoxide and then treated with perchloric or hydrochloric acid, compound (LVII) is formed. If an acid medium is avoided in the cyclisation reaction, the neutral deprotonated corrin complex (LVIII) is isolated, the protonation of which by acids leads to compound (LVII). When compound (LVII) is hydrolysed in an acid medium, the nitrile group is eliminated and compound (XXXV) is formed:



In the synthesis of the cobalt complex of corrin in the presence of acetonitrile, compound (LIX), called "pseudocorrin", was formed[63]. Initially a complex with acetonitrile attached to the cobalt atom (LX) is probably formed, whereby acetonitrile is activated and fulfils the role of the imino-ether group of ring *A*, which attacks the exocyclic methylene group:



In the absence of acetonitrile the reaction of the sodium salt (LV) with cobalt perchlorate leads, after treatment with cyanide ions and aeration, to the neutral complex (LXI), which cyclises to the dicyanide (LXII) under the action of potassium t-butoxide[64]:

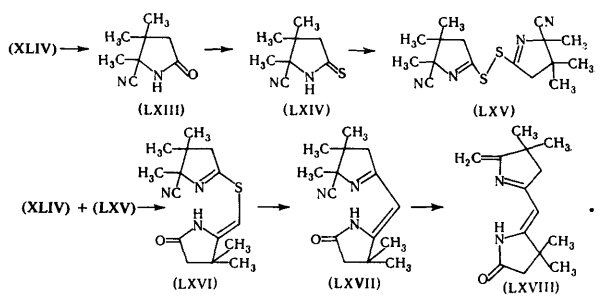


Analogous condensation of compound (L) with compound (XXXVII) results in the formation of the dicyanide of the cobalt complex of 1,2,2,7,7,12,12-heptamethylcorrin[65].

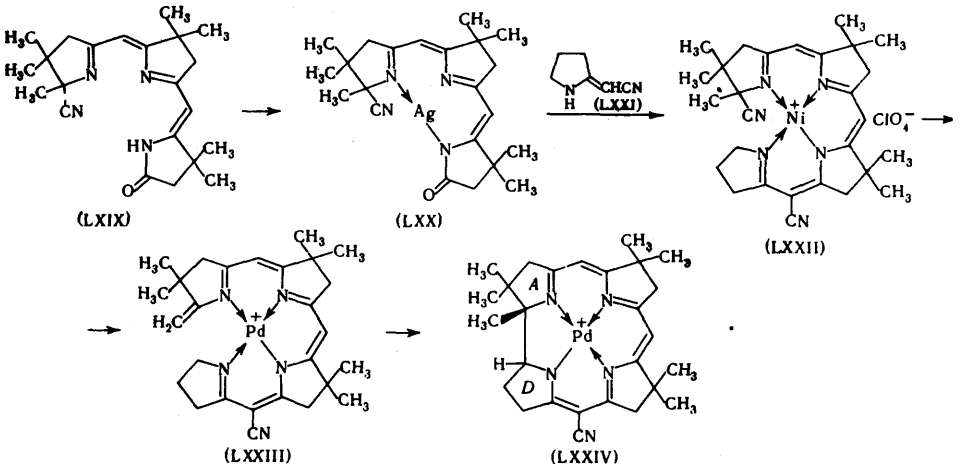
3. Synthesis of Corrins by the Introduction of a Sulphur Bridge Atom

Eschenmoser and coworkers[66] synthesised corrin also by another procedure, based on the formation of the corrin ring from monocyclic enamines and enamides by introducing a sulphur bridge atom; the final stage in this process is the photo-induced cycloisomerisation of the metal complexes of the tetracyclic system, proposed earlier by Johnson[37], and the formation of a bond between rings *A* and *D*.

Before introducing the enamide (XLIV) into the condensation reaction, the active C=C bond is protected by converting compound (LXIII) into the cyano-lactam (XLIV), the reaction of which with P_2S_5 yields the thiolactam (LXIV). The final oxidative formation of the sulphide bridge between the thiolactam (LXIV) and the enamide (XLIV) takes place under the action of benzoyl peroxide; this involves the intermediate formation of the di-imidazolinyl disulphide (LXV), which, under the action of an acid catalyst, undergoes an electrophilic substitution reaction with the CH_2 group of the enamide (XLIV) leading to the formation of compound (LXVI). Since the enamide (XLIV) is inert with respect to benzoyl peroxide, the formation of compound (LXVI) can be achieved in a single stage:



Scheme 2



When compound (LXVI) is heated with triphenylphosphine, compound (LXVII) is formed, which, after elimination of the CN group, is converted into the bicyclic lactam (LXVIII). Repetition of the process makes it possible to add to the lactam (LXVIII) a further molecule of compound (LXIV) and obtain the tricyclic lactam (LXIX). To introduce the fourth ring, the silver complex (LXX) is synthesised, in which the two nitrogen atoms are protected by being linked to silver. The reaction of the complex (LXX) with triethyloxonium tetrafluoroborate and subsequent condensation with pyrrolidine (LXXI) yields a tetracyclic compound, which is isolated as the perchlorate of the nickel complex (LXXII); under the action of palladium acetate in the presence of potassium cyanide, this compound is converted into the palladium complex and, after the elimination of the protective CN group, compound (LXXIII) is obtained, which cyclises quantitatively under the action of ultraviolet radiation or sunlight with formation of the palladium complex of 15-cyano-1,2,2,7,7,12,12-heptamethylcorrin (LXXIV) (see Scheme 2).

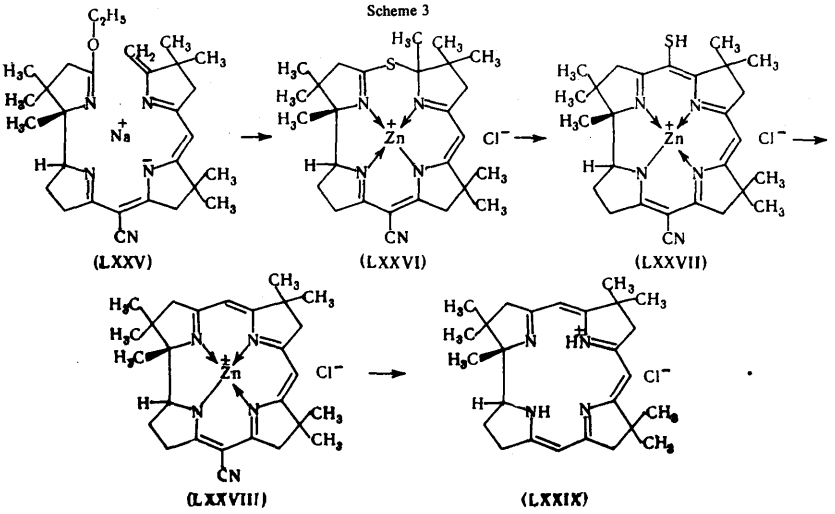
The structure of compound (LXXIV) was established on the basis of infrared, ultraviolet, NMR, and mass spectra and also by synthesis from compound (L) (*A*–*D* ring system) and compound (LXVIII) (*B*–*C* ring system). The nickel complex of compound (LXXII) could not be cyclised—probably the palladium(II) ion has a high tendency towards planar coordination.

A corrin system without cobalt was isolated[67] from the photosynthesing bacterium *Chromatium* strain D; this led to the syntheses of similar compounds. The synthesis is based on the formation of an amidine system with the intermediate introduction of a sulphur bridge atom[68].

In contrast to the imino-ether method for the synthesis of the corrin system, in the presence of a sulphur bridge atom it is not necessary to fix the ligand system into a rigid metal complex and it is possible to employ the labile zinc complex, from which the zinc ion can be readily removed in an acid medium.

Under the action of hydrogen sulphide in an acid medium, the tetracyclic compound (LXXV)[65] is converted into a thiolactam derivative, which is isolated as the zinc complex (LXXVI); without isolation of the intermediates, the latter is converted into the complex (LXXVII) by means of the following reactions: (a) oxidation with benzoyl peroxide in the presence of trifluoroacetic acid; (b) heating with trifluoroacetic acid in the presence of ethylenediaminetetra-acetic acid; (c) treatment with zinc perchlorate.

Scheme 3



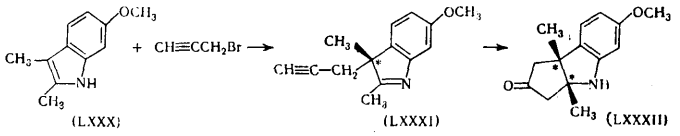
Probably trifluoroacetic acid converts compound (LXXVI) into an open-chain thiolactam which is oxidised by benzoyl peroxide, the sulphur atom being transferred to the methylene group of ring *B*; heating in the presence of ethylenediaminetetra-acetic acid results in the formation of the corrin chromophore; at the beginning of this process the intermediate breakdown of the complex ligand system probably takes place (Scheme 3).

Under the action of triphenylphosphine, the complex (LXXVII) is smoothly converted into compound (LXXVIII), the treatment of which with trifluoroacetic acid leads to the hydrochloride of the corrin base (LXXIX).[68]

4. Studies on the Stereospecific Synthesis of the Corrin Ring in Cobyrinic Acid

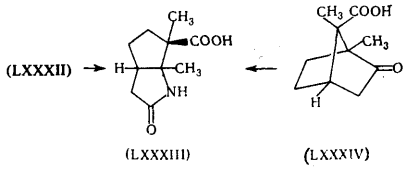
The corrin ring of vitamin B_{12} contains nine asymmetric centres, six of which are in the *A*–*D* ring system. To synthesise the corrin ring of vitamin B_{12} in which eight substituents have the correct absolute orientation, Woodward and Eschenmoser and coworkers obtained compounds which consist of rings *B* and *C* and the *A*–*D* ring system in an optically active form with the corresponding absolute specific configuration[57].

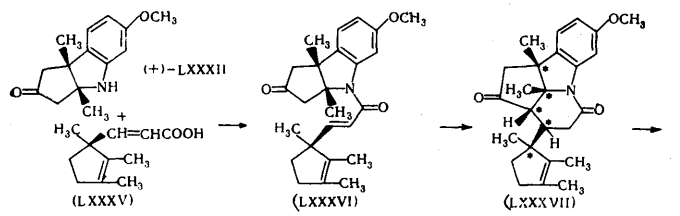
Rings *A*–*D* were obtained from methoxydimethylindole (LXXX).[69] The first asymmetric centre was produced by the reaction of the magnesium derivative of indole (LXXX) with propargyl bromide. Under the action of boron trifluoride and mercury(II) oxide in methanol, propargylindolenine (LXXXI) cyclises stereospecifically, yielding a tricyclic ketone (LXXXII) and forming the second asymmetric centre:

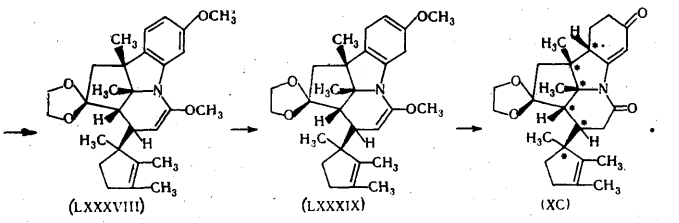


The tricyclic ketone (LXXXII) was separated into optical isomers by crystallising the diastereoisomeric ureas formed by the reaction of the racemic compound (LXXXII) with optically active α-phenylethyl isocyanate.

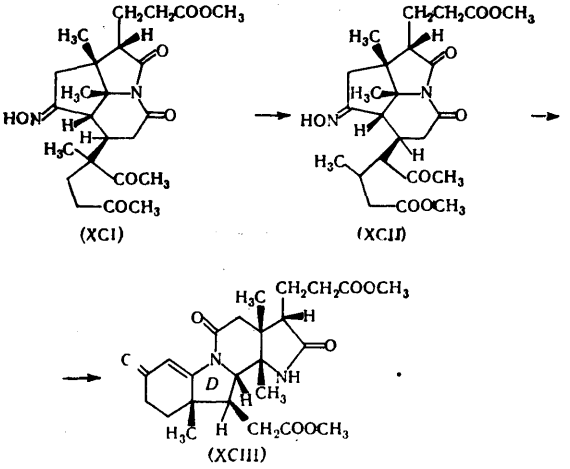
The absolute configurations[57] of the tricyclic ketones (LXXXII) were established by converting the laevorotatory isomer of compound (LXXXII) into the acid (LXXXIII) derived from the tricyclic lactam, which had been obtained from the keto-acid (LXXXIV) with known absolute configuration:



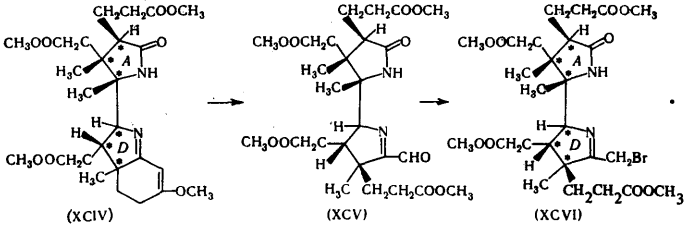




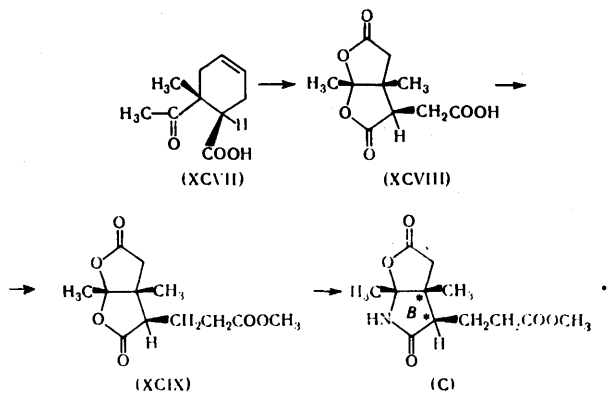
When the dextrorotatory tricyclic ketone (LXXXII) was condensed with the laevorotatory acid (LXXXV), the amide (LXXXVI) was formed, which, on treatment with potassium t-butoxide, gave the pentacyclic lactam (LXXXVII) containing two new asymmetric centres. To protect the active oxo- and carbamoyl groups, compound (LXXXVII) was converted into the ketal of the methoxyenamine (LXXXVIII), which was converted by treatment with lithium in liquid ammonia into the dihydro-derivative (LXXXIX). Acid treatment of compound (LXXXIX) yields the pentacyclenone (XC) with formation of the sixth and last asymmetric centre necessary for the synthesis of the *A*–*D* ring. To introduce a second nitrogen atom into the pentacyclenone (XC) molecule, the protecting ketal group is removed with formation of an oxime, the treatment of which with ozone and then iodic (HIO_3) acid and diazomethane converts it into compound (XCI). This substance is then converted into the keto-ester (XCII), the Beckmann rearrangement of which yields compound (XCIII) with two five-membered nitrogen-containing rings *A* and *D*:



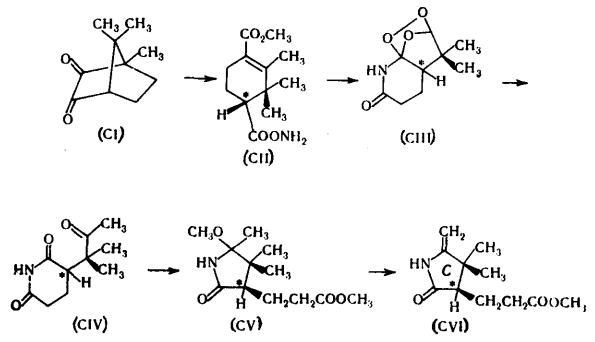
By heating compound (XCIII) with an excess of a base, acidifying, and treating with diazomethane, an isomer differing from compound (XCIII) by the orientation of the propionic acid chain was obtained. Its treatment with a methanol solution of hydrogen chloride leads to compound (XCIV), which, on reaction with ozone, subsequent acidification, and treatment with dimethyl sulphide gives rise to the aldehyde (XCV). The latter is converted into the bromide (XCVI), which constitutes the left-hand half of the vitamin B_{12} molecule:



The synthesis of ring *B* was begun with the condensation of β-acetyl-β-methylacrylic acid with butadiene leading to the cyclohexenecarboxylic acid (XCVII), which was separated into optical isomers by crystallising its salts with optically active α-phenylethylamine. Oxidation of the dextrorotatory acid (XCVII) gave the dilactone acid (XCVIII). By lengthening the acetate chain, the acid (XCIX) was obtained, which, after treatment with ammonia, was converted into the lactam (C), i.e. ring *B*. The absolute configuration of compound (C) was established by converting it into succinimide, the product of the ozonolysis of heptamethyl cobyrinate:

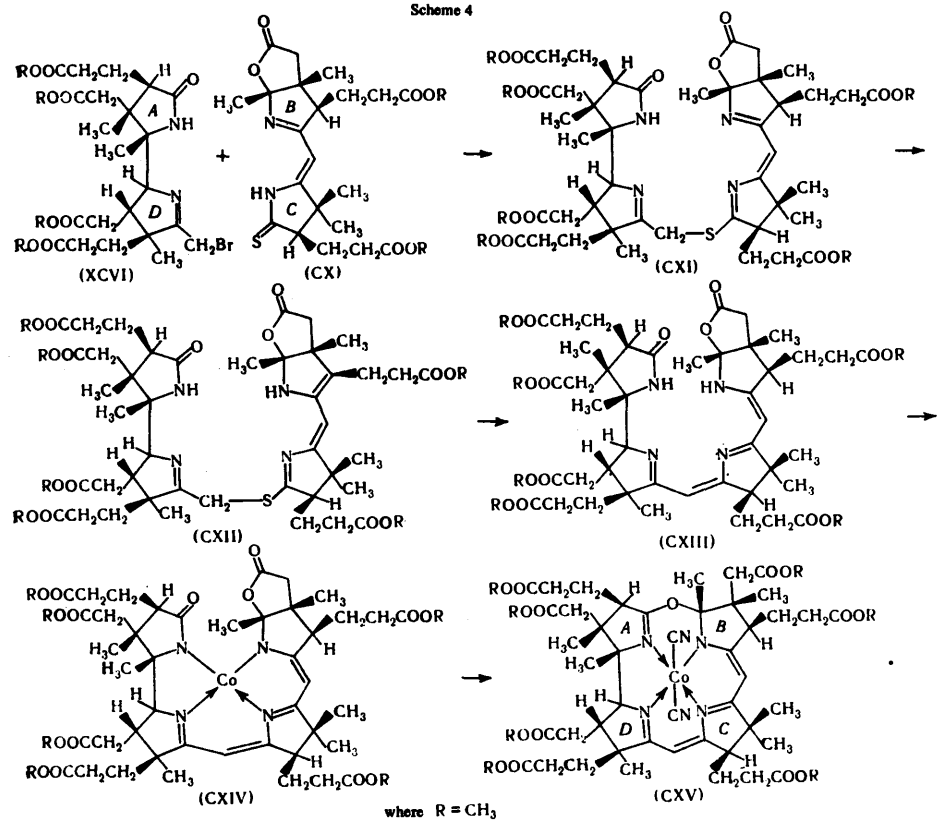


Ring *C* was synthesised from the dextrorotatory camphorquinone (CI), which was converted by a number of reactions into the amide (CII) with formation of the asymmetric centre of the required absolute configuration. Treatment of this amide with ozone leads after a number of reactions to the ozonide (CIII), the reduction of which yields compound (CIV) and the latter is converted in an acid medium into compound (CV). Finally pyrolysis of compound (CV) gives rise to the lactam (CVI), which constitutes ring *C*:

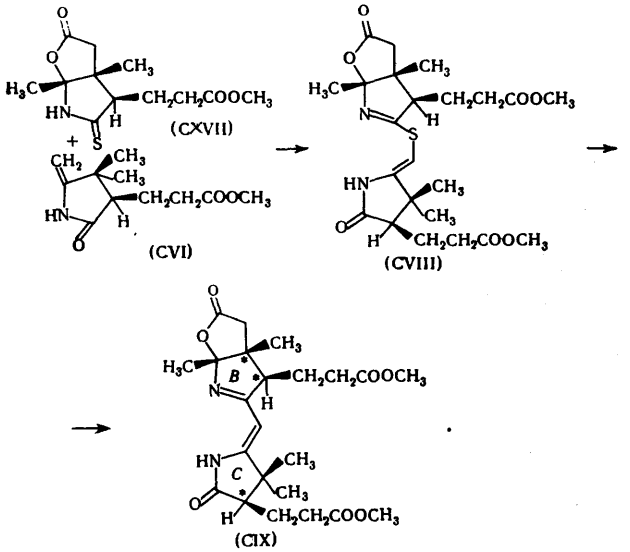


Rings *B* and *C* are joined by the introduced of a sulphur bridge atom [66] (see p. 933). The lactam (C) (ring *B*) is first converted into the thiolactam (CVII). Treatment of compound (CVII) and the enamide (CVI) (ring *C*) with benzoyl peroxide results in the formation of the S-bridge derivative (CVIII), which, on heating with $(C_2H_5O)_3P$, is converted into compound (CIX), constituting the *B*–*C* ring

Scheme 4



system with all the substituents having the correct absolute configuration:



For condensation into corrin, compound (CIX) was converted into the thiolactam (CX), which combines with the bromide (XCVI) in the presence of potassium t-butoxide with formation of the very labile sulphide (CXI). Under the action of aluminium oxide, compound (CXI) is converted into the isomer (CXII), which is desulphurated by treatment with diphenylphosphine, yielding compound (CXIII). The reaction of compound (CXIII) with cobalt perchlorate in acetonitrile in the presence of di-isopropylethylamine yields the cobalt derivative (CXIV). However, treatment of compound (CXIV) with triethyloxonium tetrafluoroborate gave the cyclic ether (CXV) instead of the expected corrin (see Scheme 4).

There is no doubt that cobyrinic acid will be synthesised in the near future.

III. PROPERTIES OF CORRIN SYSTEMS

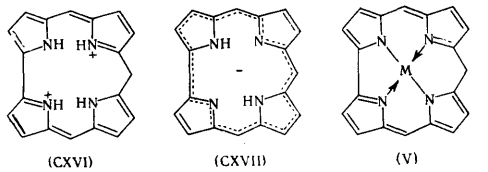
The chemical and physical properties of synthetic corrins, tetradehydrocorrins, and corroles have been little investigated§. Corrin compounds, both as free bases and metal complexes, are crystalline, intensely coloured, high-melting substances. They are sparingly soluble in water and organic solvents and readily soluble in chloroform.

The corrin ring without a metal is a base of moderate strength[68] with a pK of 8.6 (in the 4 : 1 dimethylcellosolve–water solvent).

A. CHEMICAL PROPERTIES

1. Formation and Properties of Metal Complexes

Free corrin systems (corroles and corrins) readily form metal complexes. Under the action of concentrated sulphuric or trifluoroacetic acid, the corrole (IV) [35] is converted into the non-aromatic dication (CXVI), from which the initial corrole is regenerated by treatment with alkali. The addition of dilute alkali to corrole solutions leads to the formation of the stable aromatic anion (CXVII). When corrole is treated with solutions of nickel or cobalt salts in the presence of ammonia, the corresponding metal complexes (V) are formed, the principal structural unit of which is a non-aromatic base corresponding to the dication (CXVI):



The reaction of corrin hydrochloride (LXXIX) with an excess of $Co[(CH_3)_2NCHO]_6[ClO_4]_2$ in acetonitrile yields, after oxidation with air and treatment with cyanide ions, the dicyanide of the cobalt complex 15-cyano-1,2,2,7,7,12,12-heptamethylcorrin[68].

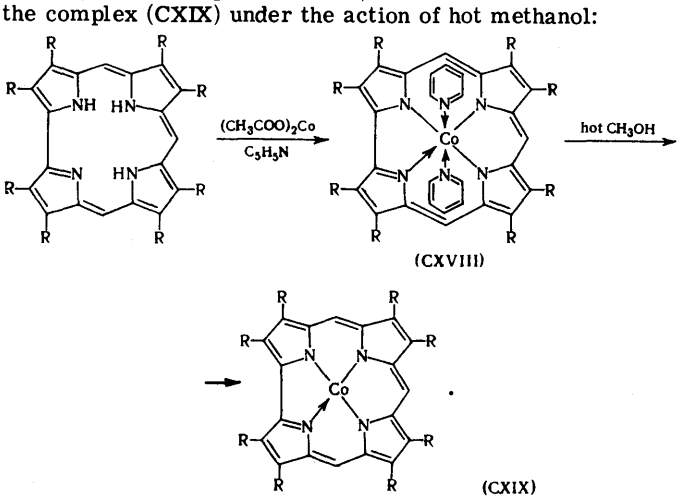
The cobalt and nickel complexes of corrins and 1,19-dimethyltetradehydrocorrins are extremely stable; the metal atom cannot be removed by treatment with strong acids and alkalis[21,47,56]. In this respect the complexes resemble natural cyanocobalamin[2].

Corrin systems are stable. Only two cases of the rupture of the tetracyclic macroring are known: the conversion of 1,19-dialkyltetradehydrocorrins on heating in *o*-dichlorobenzene into porphyrins[23,51] and the oxidation of the nickel complex of 1-methyltetradehydrocorrin to the lactam (XXII) by chromatography on alumina[51]. The mechanism of the oxidation was not established—possibly the 19-hydroxy-1-methyl derivative is formed initially and then converted into the lactam.

In contrast to the cobalt and nickel complexes, the zinc complex of corrin[68] is fairly labile, liberating the metal in an acid medium at room temperature and yielding the hydrochloride of the free base.

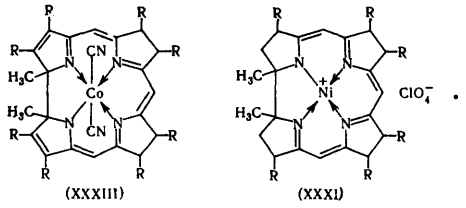
The nickel, cobalt, and copper complexes of corrole are relatively stable[35]. Their solutions are green, becoming red on treatment with alkali with the appearance of a Soret band in the ultraviolet spectra, which indicates the formation of an aromatic system.

The capacity of the cobalt atom to form octahedral complexes is responsible for the high reactivity of the cobalt complexes of corrin systems. The treatment of corrole with cobalt acetate in pyridine[36] results in the formation of the dipyridine complex (CXVIII), which is converted into the complex (CXIX) under the action of hot methanol:



§ The properties of synthetic corrin systems only are considered in the present review. The chemical and physical properties of cobalamins are deal with in other reviews[2,17].

When cobalt complexes of corrin[64] and 1,19-dimethyltetradehydrocorrins[47] are treated with cyanide ions, the corresponding dicyano-compounds are formed. The reduction of the dicyanide (XXXIII) with sodium borohydride followed by treatment with methyl iodide gives rise to spectroscopic changes corresponding to the formation of a derivative with a cobalt–methyl bond. This compound is readily photolysed and after treatment with sodium cyanide is reconverted into the initial complex (XXXIII):



(XXXIII) (XXXI)

The nickel complex (XXXI) is known to react with methyl iodide in an alkaline medium[63], but the structure of the product formed has not been established.

2. Deuterium Exchange

Deuteration of all types of corrinoid systems has been investigated—corrole[35], the nickel complex of 1-methyltetradehydrocorrin[51], and also the nickel and cobalt complexes of corrin[70].

All three *meso*-protons of corroles are rapidly exchanged for deuterium in deuterotrifluoroacetic acid[35], in contrast to porphyrins[71] where there is no exchange in the *meso*-positions under analogous conditions.

The *meso*-protons of the nickel complex of 1-methyltetradehydrocorrin are also exchanged in an acid medium. It was found that in a 0.25 M solution of the complex in deuterotrifluoroacetic acid at 35°C the period required for 50% exchange of the proton in the 10-position is 15 min and that for the protons in the 5- and 15-positions is 11 min[51].

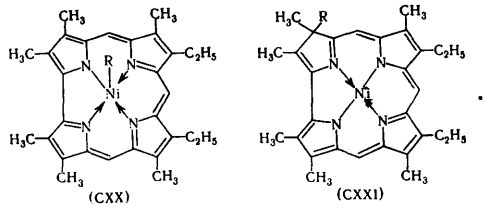
When the dicyanide of the cobalt complex of corrin is deuterated in an acid medium (pD 2, 5 days),[70] all three vinyl *meso*-protons are also exchanged but the allyl protons are not. When the duration of the deuteration process is reduced to 24 h, partial deuterium exchange takes place, preferentially in the 15-position.

The base-catalysed deuteration of the cobalt and nickel complexes of corrins[70] takes place selectively in the 8-position, i.e. the exchange takes place only in the allyl methylene group of ring *B*. The deuteration of the dicyanide of the cobalt complex of corrin under the action of the (1 : 1 t-C_4H_9OD–D_2O)–NaOD–KCN system (concentration of complex 0.071 M, pD 12, duration 7 h, temperature 31°C) is a first-order reaction with respect to corrin, the time required for 50% exchange being 99 ± 5 min. The exchange of protons in the 8-position of the nickel complex of corrin takes place even in the presence of a weak base (1 : 1 pyridine–D_2O, 15 h).

3. Some Reactions of the Corrin Ring

Of the electrophilic substitution reactions in corrin systems, only the cyanation of the nickel and cobalt complexes of corrins[70] and the alkylation of the nickel complexes of corroles[72] and 1-methyltetradehydrocorrins[73] have been investigated. The reaction of the dicyanide of the cobalt complex of corrin with three equivalents of chlorosulphonyl isocyanate followed by treatment with dimethylformamide leads to the 15-cyano-derivative. The cyanation of nickel complexes of corrin and 8,8-dideuteriocorrin[70] also takes place in the 15-position.

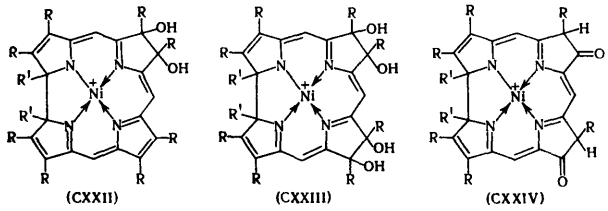
The alkylation of the nickel and cobalt complexes of 1-methyltetradehydrocorrins[73] with alkyl halides involves the 19-position, which results in the formation of salts of the complexes of 1,19-dialkyltetradehydrocorrins[23,51,73]. Methyl, ethyl, n-propyl, allyl, and benzyl groups were introduced in this way into the 19-position. The methylation of corrole[35] under the action of methyl iodide leads to the formation of a mixture of two *N*-methyl derivatives. The alkylation of the nickel complexes of corrole[72] involves the nickel atom with formation of an Ni–C bond, which yields Ni-alkyl derivatives (CXX). When compound (CXX) is heated in chlorobenzene in an atmosphere of nitrogen, a mixture of products is formed, containing the nickel complex of 3,3-dialkylcorrole (CXXI):



(CXX) (CXXI)

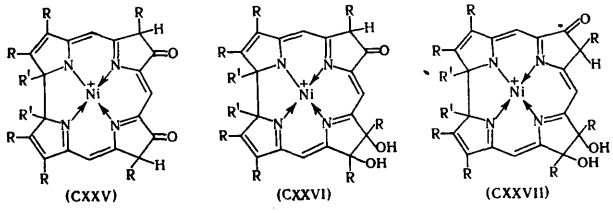
When allyl bromide is used as the alkylating agent[72], the nickel complex of *gem*-allylmethylcorrole (CXXI, R = $CH_2CH=CH_2$), which may be a product of the rearrangement of the Ni-allyl derivative, is isolated immediately.

The oxidation of the nickel complexes of tetradehydrocorrins with osmium tetroxide, leading to a mixture of 7,8-dihydroxytridehydrocorrins (CXXII) and 7,8,12,13-tetrahydroxydidehydrocorrins (CXXIII), has been investigated[74,75]:



(CXXII) (CXXIII) (CXXIV)

In the case of tetradehydrocorrins with free 2- and 18-positions, 2,3,7,8,12,13-hexahydroxydehydrocorrin and 2,3,7,8,12,13,17,18-octahydroxycorrin are formed in addition to compounds (CXXII) and (CXXIII). The pinacol rearrangement of compound (CXXIII) yields a mixture of diketones (CXXIV) and (CXXV):



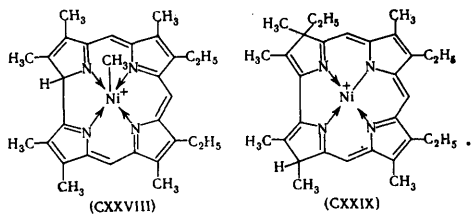
(CXXV) (CXXVI) (CXXVII)

The pinacol rearrangement of compound (CXXII) results in the formation of a mixture of monoketones, which, after treatment with OsO_4, are converted into dihydroxy-ketones (CXXVI) and (CXXVII), compound (CXXVI) being formed in

a greater amount. The structures of compounds (CXXVI) and (CXXVII) were confirmed by the products resulting from the pinacol rearrangement: compound (CXXVI) gives a mixture of compound (CXXIV) and compound (CXXV), while in the case of compound (CXXVII) only compound (CXXIV) is isolated.

Acids have different effects on the free bases of corroles and corrins and their metal complexes. The treatment of corrole with a dilute solution of hydrogen bromide in acetone leads to the formation of a monohydrobromide[34,35], in contrast to porphyrins which give rise to dihydrobromides under similar conditions. Similarly free corrin is isolated as the monohydrochloride[68].

The treatment of the nickel complex of 1-methyltetradehydrocorrin with strong acids, for example perchloric, results in the addition of a proton in the 19-position and the formation of a salt of the nickel complex[23,51]. The deprotonated complex of corrin (LVIII) is converted into the usual corrin complex under the action of hydrochloric or perchloric acid[65]. The nickel complex of the methyl derivative of corrole (CXX) is protonated by trifluoroacetic acid in the 19-position with formation of the complex (CXXVIII), which is converted by bases into the initial complex (CXX). When the nickel complex of *gem*-dialkylcorrole (CXXI) is treated with trifluoroacetic acid, a proton adds in the 17-position with formation of the complex (CXXIX):[72]



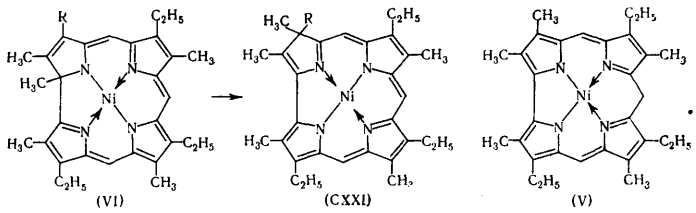
(CXXVIII) (CXXIX)

While alkylation of 1-methyltetradehydrocorrins leads to 1,19-dialkyl derivatives, there are reactions whereby 1,19-disubstituted tetradehydrocorrins are converted into corroles and 1-methyltetradehydrocorrins. The treatment of the perchlorate of the cobalt complex of 1,19-diethoxycarbonyltetradehydrocorrin with a methanol solution of sodium hydroxide at 20°C results in the hydrolysis and decarboxylation of both ethoxycarbonyl groups with formation of the cobalt complex of corrole. Similarly the nitrate of the nickel complex of 19-ethoxycarbonyl-1-methyltetradehydrocorrin is readily converted into the nickel complex of 1-methyltetradehydrocorrin[51].

In contrast to the ease of hydrolysis and decarboxylation of the 1- and 19-ethoxycarbonyl groups of tetradehydrocorrins, the hydrolysis of the 5-cyano-group of corrin complexes[56,64] with subsequent decarboxylation of the carboxylic acid formed takes place only after heating for many hours in an acid medium.

4. Rearrangements of Metal Complexes of Tetradehydrocorrins

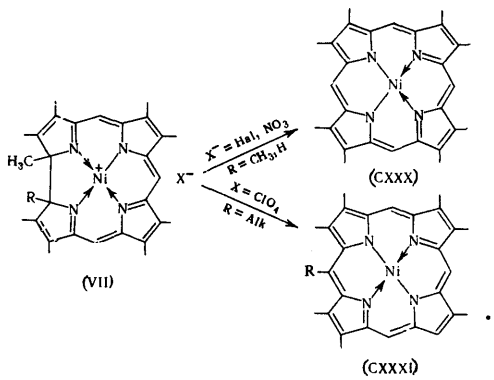
An interesting reaction of the nickel complexes of tetradehydrocorrins is their thermal rearrangement without expansion of the macroring. The nickel complexes of 1-methyltetradehydrocorrins (VI), which have a conjugated system of double bonds locked in the 1-position by an angular methyl group, are converted by refluxing in *o*-dichlorobenzene into nickel complexes of 3,3-dialkylcorrole (CXXI).[73,76] The migration of the angular methyl group from the 1- to the 3-position may be regarded as a sigmatropic shift[77]:



(VI) (CXXII) (V)

The thermal rearrangement of compound (VI) with R = H leads to the nickel complex of corrole of type (V) with formation of the acyclic lactam (XXII) as a side product. Another example of this kind of rearrangement is the formation of compound (CXXI, R = $COOC_2H_5$)[76] by heating the chloride of the nickel complex of 1,19-diethoxycarbonyltetradehydrocorrin in chlorobenzene with elimination of one ethoxycarbonyl group.

The salts of the nickel complexes of 19-alkyl-1-methyltetradehydrocorrins of type (VII) undergo the thermal corrin–porphyrin rearrangement[78] with expansion of the macroring, which leads to the formation of the nickel complexes of unsubstituted porphyrins (CXXX) or *meso*-substituted porphyrins (CXXXI):



(VII) (CXXX) (CXXXI)

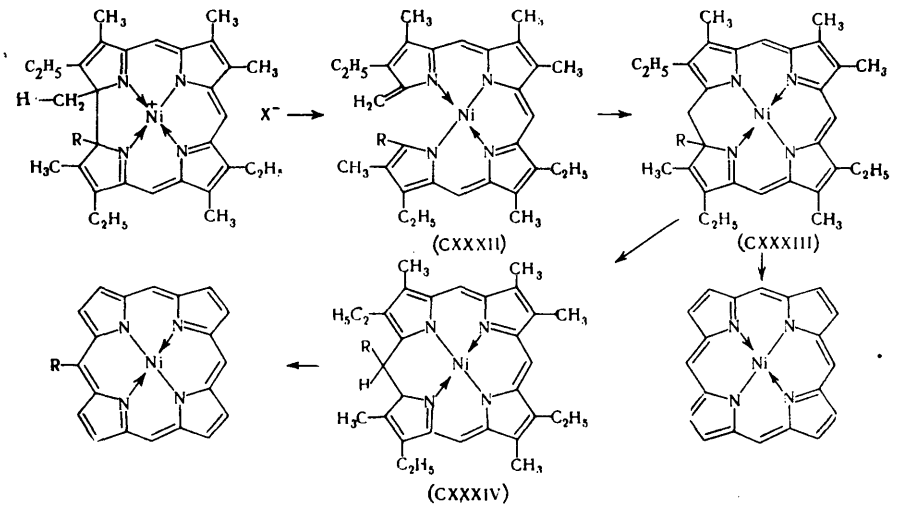
The formation of the nickel complexes of unsubstituted porphyrins takes place with elimination of an alkyl group in the rearrangement of the halides or nitrates of the nickel complexes of 19-alkyl-1-methyltetradehydrocorrins. The salts of the nickel complexes of 1,19-dimethyl- and 1-methyltetradehydrocorrins, containing any anion, give rise to the nickel complexes of substituted porphyrins, while the neutral nickel complex of 1-methyltetradehydrocorrin rearranges to 3,3-dialkylcorrole. This difference in thermal rearrangement is due to the presence of a positive charge in the macroring of salts of type (VII).

Perchlorates give rise mainly to *meso*-alkylporphyrins, formed by the migration of the alkyl group without isomerisation of its carbon framework; an exception is the 19-allyl derivative which is converted into *meso*-propenylporphyrin[78].

The first stage in the corrin–porphyrin rearrangement is the formation of an intermediate bilatriene complex (CXXXII) with elimination of a proton from the angular methyl group, the anion behaving as a base. The complex (CXXXII), containing a benzylidene instead of a methylene group, was isolated after the rearrangement of the bromide of the nickel complex of 19-benzyl-1-methyltetradehydrocorrin (see Scheme 5).

The cyclisation of compound (CXXXII)[78] leads to the complex (CXXXIII), which, after the migration or elimination of the alkyl group, is converted into a substituted or

Scheme 5



unsubstituted porphyrin. The type of porphyrin formed depends on the anion. The perchlorate ion, in the presence of which *meso*-substituted porphyrins are formed, has oxidising properties and the corrin–porphyrin rearrangement of perchlorates takes place via the cation (CXXIV).

The study of the rearrangement of the perchlorates of the nickel complexes of 1,19-dialkyltetradehydrocorrins with unsubstituted 2- and 18-positions showed that in this case the products are only *meso*-alkylporphyrins, i.e. there is no migration of the alkyl group to the adjacent free β-position.

The thermal corrin–porphyrin rearrangement of the chloride of the nickel complex of decamethyltetradehydrocorrin takes place anomalously, the product being the unsubstituted porphyrin and porphyrin oxide.

B. SPECTROSCOPIC PROPERTIES

One of the most important characteristics of tetrapyrrole macrocyclic systems is their absorption in the visible and ultraviolet regions. The electronic absorption spectra of the solutions of all corroles in chloroform have an intense absorption band at about 400 nm [30,34,35] (the Soret band) which indicates the aromaticity of the corrole ring. In concentrated sulphuric acid the Soret band disappears, i.e. corrole is converted into the non-aromatic dication (CXVI) (p. 937). The addition of dilute alkali to corrole solutions alters the spectrum, but the Soret band persists, which indicates that the anion (CXVII) is aromatic [35,36] (p. 937).

All corroles absorb at 396–399 nm (Soret band) and at 536–545, 550–553, and 592–594 nm. The Soret band persists in the spectrum of corrole hydrobromide [35] but there is additional absorption at 577 nm.

The spectra of the neutral complexes of corroles (V) (p. 937) do not contain the Soret band [35]; nickel complexes show a characteristic absorption at 360 and 659 nm, cobalt complexes absorb at 389, 499, and 528 nm, and finally copper complexes absorb at 397 and 548 nm. The salts of the nickel and cobalt complexes of 1,19-disubstituted tetradehydrocorrins (VII) (p. 927) have three characteristic absorption regions [47]: 273–278, 352–360, and 557–572 nm. The replacement of angular methyl groups by ethoxycarbonyl groups does not alter the spectrum [appreciably], the 557 nm band undergoing a bathochromic shift by 15 nm only, probably due to steric factors.

The presence of *meso*-methyl groups [47] has a considerable influence on the absorption of tetradehydrocorrins; when a *meso*-methyl group is introduced, the 557 nm band undergoes a bathochromic shift. The spectral shifts caused by the methyl group in the 10-position are equivalent to the overall effect of the methyl groups in the 5- and 15-positions; in both cases the 557 nm band is displaced by 45 nm and is located at 600 nm.

When the nickel complexes of 1-methyltetradehydrocorrins (XXI) (p. 930) are protonated by strong acids [23,47], the products are salts, the visible spectra of which are similar to those of the salts of the nickel complexes of 1,19-dimethyltetradehydrocorrins (XVIII) (p. 929). The spectra of the nickel and cobalt complexes of synthetic corrin [56,64] are typical for vitamin B_{12}. The visible spectrum of the dicyanide of the cobalt complex of 1-methylcorrin obtained by the reduction of the corresponding tetradehydrocorrin [23] coincides fully with the spectrum of cyanocobalamin [2].

Infrared spectroscopy has not been used quite as widely to characterise corrin systems. In the spectra of the nickel [56], cobalt [64], and zinc complexes of corrin and also in the spectrum of corrin hydrochloride [68] there are two intense bands in the region of the C=C and C=N absorption at 1592 and 1508 cm^{-1}, which are characteristic of the corrin chromophore and are present in the same region in the spectrum of cobyrinic acid [79].

The infrared spectra of the nitrates and perchlorates of the nickel and cobalt complexes of 1,19-disubstituted tetradehydrocorrins and also of the dicyanide of the cobalt complex of 1,19-dimethyltetradehydrocorrin [47] have been recorded; the spectra of the salts show absorption characteristic of the nitrate and perchlorate ions. In the spectra of compounds with angular ethoxycarbonyl groups there are bands at 1730–1740 cm^{-1} due to the ester carbonyl group, which is consistent with the presence in the tetradehydrocorrins of an ethoxycarbonyl group attached to an aliphatic carbon atom, while the ester carbonyl groups of biladienes, linked to unsaturated carbon atoms, absorb at 1695–1710 cm^{-1}.

Nuclear (proton) magnetic resonance spectra have been most widely used to establish the structures of tetrapyrrole macrocyclic compounds.

The NMR spectrum of 2,3,8,12,17,18-hexaethyl-7,13-dimethylcorrole[35], recorded in deuterochloroform using tetramethylsilane as standard contains a 0.88 τ singlet (5- and 15-*meso*-protons), a 1.18 τ singlet (10-*meso*-proton) a broad 13.48 τ singlet (the three protons of the NH groups), three partially overlapping quartets with the centre at 6.18 τ (the twelve protons of the methylene groups in the ethyl substituents), a 6.72 τ singlet (the six protons of the methyl groups), and three partially overlapping triplets with the centre at 8.30 τ (the 18 protons of the methyl groups in the ethyl substituents).

The NMR spectra of the chloride[36] and nitrate[47] of the nickel complex of 1,19-dimethyltetradehydrocorrin showed the following signals: a 9.34 τ singlet (the two angular methyl groups), a 2.41 τ singlet (the three *meso*-protons), a 7.30 τ singlet (the six methyl groups), and 8.54 τ triplet (the two methyl groups in the ethyl substituents), and a 6.83 τ quartet (the two methylene groups in the ethyl substituents).

The abnormally high signal due to the angular methyl groups (9.34 τ) is caused by the closeness of the $\beta\beta$-double bonds of the adjacent *A* and *D* rings, although it may be the result of the increasing drawing together of the cyclic system in consequence of the sp^3 hybridisation of both the 1- and 19-carbon atoms. The positive charge of the metal in the salts of 1,19-dimethyltetradehydrocorrins can lead to the de-screening of the protons of the 1- and 19-methyl groups, but this effect should be slight. In support of this hypothesis, one may say that neither vitamin B_{12} [80] nor synthetic corrin[56], which do not have a $\beta\beta$-double bond in rings *A* and *D*, give rise to signals in excess of 9 τ.

According to steric considerations the 1- and 19-substituents should be located on the opposite sides of the macroring.

The planar salts of the cobalt complexes of 1,19-dimethyltetradehydrocorrins are paramagnetic but the dicyanide octahedral complex[47] has a spectrum in which the angular methyl groups give rise to a signal of 9.26 τ.

The introduction of a 10-*meso*-methyl group results in a 6.83 τ singlet characterising this group, and reduces the intensity of the 2.55 τ singlet (two *meso*-protons), the remaining signals being unchanged. The spectrum of the nickel complex of 1,5,15,19-tetramethyltetradehydrocorrin reveals the presence of only one *meso*-proton (2.50 τ singlet), the 5- and 15-methyl groups giving rise to a 6.82 τ singlet and the two angular methyl groups to a 9.42 τ singlet[47].

The spectra of all the neutral nickel complexes of 1-methyltetradehydrocorrins[23,50,51] have an 8.5 τ singlet due to the three protons of the angular methyl group. The angular groups of the nickel complexes of 1-ethyl- and 1-isopropyl-tetradehydrocorrins[51] are characterised by 9.59 τ (ethyl) and 9.58 τ and 9.55 τ (isopropyl) singlets. The shielding of the angular alkyl groups can be accounted for by their closeness to the π-electron system of ring *A*, the degree of shielding depending strongly on the dimensions of the angular groups.

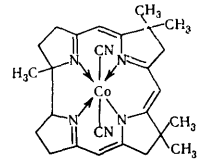
The protonation of the nickel complexes of 1-methyltetradehydrocorrins by strong acids results in the formation of salts the angular methyl groups of which are characterised by a 9.38 τ singlet[50] and the proton in the 19-position by a 6.73 τ singlet[51]; as for the metal complexes of 1,19-dimethyltetradehydrocorrins, the high signal due to the angular methyl group is caused by its interaction with the $\beta\beta$-double bond of the adjacent ring.

In the spectra of the nickel complexes of 1-methyltetradehydrocorrins[51] with several β-methyl substituents, the signal of one of them is at 8 τ, while those of the remaining methyl groups are at 7.6–7.8 τ. The study of the NMR spectra of many metal complexes of 1-methyltetradehydrocorrins with β-methyl substituents in various positions led to the conclusion that the shift of the signal to 8 τ is caused by the methyl group in the 3-position. Molecular models show that the substituents cluster together near the 1-, 2-, 18-, and 19-positions, i.e. the direct bond between rings *A* and *D* is protected.

The signals due to the *meso*-protons of the neutral nickel complexes of 1-methyltetradehydrocorrins[51] are at 2.8, 3.0, and 4.0 τ, while the analogous signals of the salts are at 2.4–2.5 τ (C_{10}) and 2.65–2.8 τ (C_5 and C_{15}). The lower chemical shift of the signals due to the *meso*-protons shows that the deshielding effect of the nickel cation is directed to the *meso*-positions. For example, the three *meso*-protons of the salts of the nickel complexes of 1,19-dimethyltetradehydrocorrins give rise to one or two singlets at 2.5 τ,[47] in contrast to porphyrin salts[81].

The signal due to the *meso*-proton of the nickel complex of 1-isopropyltetradehydrocorrin at 2.88 τ has the form of a sharp singlet, while the other two *meso*-protons give rise to very broad signals at 3.3 and 4.13 τ; the *meso*-protons of the nickel complex of 1-methyltetradehydrocorrin are characterised by three sharp singlets. Possibly in 1-isopropyltetradehydrocorrin the conformation equilibrium is established slowly along the axis passing through C_{10} and the C_1-C_{19} bond, similarly to the analogous effect in annulenes[82].

In the NMR spectra of the nickel and cobalt complexes of corrin[56,65] the positions, structures, and intensities of all the signals correspond to the following hypothetical molecular structure:



In the NMR spectrum of the dicyanide of the cobalt complex of corrin[70] in $CDCl_3$ there are signals due to five methyl groups, two non-allylic methylene groups, four allylic methylene groups, and three vinyl *meso*-protons, which are characterised by singlets at 4.60, 4.56, and 4.44 τ; the last refers to the proton in the 15-position and is very broad due to the spin–spin interaction with the protons of the allyl group of ring *C*, the signal of which is also a diffuse singlet at 7.16 τ. The methylene group in the 8-position is characterised by a singlet at 7.09–7.07 τ and the methylene groups in the 3- and 17-positions are characterised by a multiplet at 6.9 τ.

In the NMR spectrum of the nickel complex of corrin the *meso*-proton in the 15-position gives rise to a weak triplet; it has been established by the double resonance method that the triplet is due to the spin–spin interaction of the *meso*-proton with the methylene group of ring *C*.

The NMR spectra of the corrins (XXXI) and (XXXIV) [23] (p. 931), obtained by the hydrogenation of tetradehydrocorrins, show that none of the β-methyl groups is [part of] an olefinic substituent: the three *meso*-protons of corrin (XXXI) give rise to singlets at 3.93 and 4.04 τ and the *meso*-protons of compound (XXXIV) are characterised by a broad singlet at 4.5 τ.

As already noted, NMR spectroscopy is the principal method for the establishment of structures of tetrapyrrole macrocyclic compounds. This is particularly true as regards the determination of the structures of the reduction products of tetradehydrocorrins.

In the studies on the synthesis of corrins a number of tetrapyrrole macrocyclic compounds with different degrees of unsaturation were isolated. The metal complex (XXIV)[53] (p. 930), which has nine double bonds, is characterised by three singlets between 7.45 and 7.69 τ (aromatic methyl group), two doublets at 8.38 and 8.62 τ (aliphatic methyl group), and a singlet at 8.8 τ (angular methyl group).

The chelate complexes (XXVI),[53] (XXXII),[63] and (XXXIII)[47] (pp. 930 and 931) each contain eight eight double bonds. In the NMR spectra of these compounds there are signals due to the three *meso*-protons (singlets at 2.41–3.13 τ) [in the case of compound (XXVI) one *meso*-proton gives rise to a doublet] and signals arising from the methyl groups attached to the unsaturated carbon atoms (singlets at 7.55–7.75 τ). In the spectrum of compound (XXVI) there are singlets at 8.31 and 8.43 τ produced by the *gem*-methyl groups.

Compound (XXIX) contains seven double bonds[47] (p. 931). The spectrum of this compound is very complex, but certain assignments have been made: the *meso*-protons are characterised by three singlets near 4.4 τ, which coincide with the signals from the synthetic nickel complex of corrin[56]; the intensity ratios are not 1 : 1 : 1, probably because of the presence of several stereoisomers. The 7.97 τ singlet is due to the protons of the two olefinic methyl groups, which indicate the retention of the $\beta\beta$-double bond in ring *A* or *D*. The 9.22 τ singlet, corresponding to three protons, suggests the screening of one angular methyl group by the $\beta\beta$-double bond of an adjacent ring. Finally a complex series of peaks at 8.6–9.1 τ characterise the β-methyl groups attached to the aliphatic carbon atoms and the signals at 6.7–7.4 τ characterise the β-protons of the reduced rings.

In conclusion it should be noted that the development of the chemistry of corrin systems is still in the initial stage. Future studies will undoubtedly reveal many interesting and important facts in this field as well as theoretical generalisations, which will make it possible to synthesise natural biocatalytic systems and biologically active structures similar to them.

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All-Union Vitamins Research Institute, Moscow

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Catalytic Properties of Rhenium and Its Compounds

M.A.Ryashentseva and Kh.M.Minachev

The most promising applications of rhenium are in electronics, radio technology, electrical technology, and the vacuum electronics industry. The present review deals with the application of rhenium and its compounds as catalysts for various reactions in organic synthesis. 107 references.

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I. INTRODUCTION

Since its discovery in 1925, rhenium has claimed a special place among the rare elements[1,2]. Its existence was predicted by Mendeleev, who called the element dvi-manganese. Rhenium belongs to Group VII of the Periodic Table, with atomic number 75, atomic weight 186.3, atomic radius 1.361 Å, and a hexagonal lattice with lattice parameters $a = 2.765$ Å, $c = 4.470$ Å, $c/a = 1.61$. Its melting point (3170°) is the third highest after diamond and tungsten, and its physical properties are similar to those of the refractory metals of Group VI. Due to the presence of five electrons in the 4*d* shell, which are available for covalent bond formation in addition to the two 6*s* electrons, rhenium is a fairly reactive element. The chemical properties of rhenium are similar to those of the Group VII metals (in particular, manganese). The metal is stable towards oxidation and shows remarkable corrosion resistance in moist and aggressive ambients. The most stable oxygen, sulphur, and selenium compounds of rhenium are those in which the element has a valence of four or seven (ReX_2 and Re_2X_7, where X = O, S, Se). Several reviews of the chemistry of rhenium and its compounds have appeared[3-19].

Rhenium is used at present as an electrical contact material, for metallic coatings, for alloys having special physical properties, as an additive in corrosion-resistant alloys, etc. The demand for rhenium and rhenium salts is increasing continuously in the USSR as well as in the USA, Germany, Britain, and France.

The production of rhenium in the USA had reached 1000 tons per annum in 1957[17], the main deposits of rhenium being found in that country. In countries where platinum resources are inadequate, the search for alternative catalysts is an urgent problem: rhenium offers attractive possibilities in this direction. The fact that rhenium lies close to the platinum group metals in the Periodic Table suggests comparable catalytic properties in the presence of hydrogen: in particular, the ability to catalyse hydrogenation and dehydrogenation reactions, activation of unsaturated bonds, promoting action, etc. The properties of rhenium supported on various carriers are being extensively studied. When producing a catalytically active surface it is important to choose a metal which will not suffer recrystallisation during the catalytic reaction. Hence, metals with a high melting point and resistant to ageing effects are particularly valuable. Rhenium is very promising in this respect because of its high melting point and its closely packed structure.

No systematic investigation of the catalytic properties of rhenium was published until the 1930's, the only information being found in the Patent literature. The recent discovery of the element, and the high cost of its production, may have been responsible for the lack of open publications.

Thus, the use of rhenium as a catalyst for the chlorination of methane to chloroform, and of rhenium sulphide on active carbon for the dehydrogenation of fuel oils under pressure and for the synthesis of ammonia, is disclosed in a number of Patents[20-28]. Deuterium can be obtained from D_2O by exchange with hydrogen in the presence of Re_2S_7. Rhenium oxide and rhenium salts have been proposed for the oxidation of sulphur dioxide to sulphur trioxide; colloidal rhenium (in large excess) has been used for the reduction of the double bonds in maleic and cinnamic acid. Fast isotope exchange between water and deuterium has been reported on a rhenium heptasulphide catalyst supported on carbon[29]. The replacement of deuterium by hydrogen in heavy water occurs also in the presence of metallic rhenium[30,31]. Rhenium is not normally used as an oxidation catalyst because its oxides are too volatile in an oxidising medium[32]. However, telluric oxide containing 5% of rhenium oxide[33] is used for the selective oxidation of methyl or methylene groups adjacent to a double or a triple bond by a phenyl radical or hydroxyl group. In the oxidation of propene by air to acrolein[34,35], the yield is ~16% on a catalyst containing rhenium oxide as compared with ~2% on a catalyst without rhenium oxide. Alloy catalysts have a high activity in the vapour-phase oxidation of sulphur dioxide to sulphur trioxide[36,37]. Small additions of rhenium to these catalysts increase their catalytic activity and improve their stability towards poisoning. Thus, tungsten is relatively inactive towards the oxidation of sulphur dioxide to sulphur trioxide, but it becomes active when alloyed with 10% of rhenium. In the presence of this alloy, supported on glass wool, the extent of reaction is 75%, whereas it is only 30% when the rhenium is omitted. In the oxidation of ammonia[34,35] a platinum–rhenium alloy gives a higher yield of product than does the simple platinum catalyst as

well as showing higher uniformity and resistance to poisoning. In aqueous solutions[33] rhenium oxide can be used for the oxidation of nitrites to nitrates and sulphites to sulphates.

Tropsch and Kassler[38,39], who studied the hydrogenation of ethylene to ethane and the production of methane from CO_2 and H_2, and demonstrated the large increase in activity resulting from the addition of rhenium to a copper catalyst, also published their work in the 1930's. These authors suggested the possibility of hydrogenating unsaturated hydrocarbons containing not less than three carbon atoms. Schmidt[40] pointed out that rhenium is inferior to platinum, palladium, and nickel in dehydrogenating power.

Evidently, only fragmentary knowledge of the catalytic properties of rhenium was available in the 1930's. During the 1940's, and particularly since 1960, intensive studies of the catalytic properties of rhenium began, both in the Soviet Union and abroad, concurrently with the greater availability of the element.

II. RHENIUM AND ITS OXYGEN, SULPHUR, AND SELENIUM COMPOUNDS (dehydrogenation of alcohols and reduction of various organic compounds)

Platonov and coworkers[41-49] showed that finely divided rhenium at room temperature is relatively inactive towards the hydrogenation of maleic acid and cyclohexene. On raising the temperature to 250° the element catalyses the hydrogenation of benzene, cyclohexene, nitrobenzene, and nitric oxide. Up to 22% of cyclohexane is formed from cyclohexene[41]. A simple method of preparing rhenium in a disperse and active form from ammonium perrhenate — the "nitric acid" method — has been described[41]. Acetone was obtained in 85% yield by dehydrogenation of isopropanol on a finely divided rhenium catalyst[42,43] at 400°; from n-propanol, propionaldehyde was obtained in 20.8% yield. Isopropanol is dehydrogenated much more readily than n-propanol on a rhenium catalyst[43], but not so readily as n-butanol[44]. The dehydrogenation of isopentanol has also been investigated[45]: no side-products (acids, esters, unsaturated compounds) are found in the catalysis product. Cyclohexanol at 450° gives[47] up to 25% of cyclohexanone, and small amounts of cyclohexene, benzene, and a trace of phenol. Known alcohol dehydrogenation catalysts, such as platinum, nickel, zinc, and copper, were shown to have a lower activity and selectivity.

The dehydrogenation properties of rhenium catalysts have been studied[45] by examining the decomposition of formic acid ($HCOOH \rightarrow CO_2 + H_2$). The activity of the rhenium catalyst was found to be comparable to (or higher than) the activity of spongy Pt, Pd, and Cu catalysts. The percentage decomposition to CO_2 and H_2 was 8.7, 57.5, 100, and 100% at 100, 175, 230, and 250° respectively.

Broadbent and coworkers[50-55] studied the catalytic activity of rhenium catalysts in the liquid-phase hydrogenation of over 100 organic compounds. The following rhenium compounds were used as catalysts: (A) rhenium black, prepared by reduction of Re_2O_7 *ex situ*; (B) rhenium black, prepared by reduction of Re_2O_7 *in situ*[50]; (C) Re_2O_3, reduced by sodium borohydride[51]; (D) the tetrahydropyran complex of Re_2O_7[52]; (E) $ReO_2 . 2.5H_2O$[53]; (F) ReO_3[54]; (G) $ReO.2H_2O$.[55] Optimum reduction conditions were identified (temperature, pressure, and time), and suitable solvents were chosen. The properties of these catalysts are compared in Table 1, which lists only cases in which the yield was practically quantitative.

It is evident from Table 1 that many of the rhenium catalysts have considerable activity. By choosing comparable hydrogenation conditions (temperature, reaction time, and pressure), the best catalysts can be identified. For example, the best catalyst for the reduction of hex-1-ene to hexane is *in situ* rhenium black (B); for the reduction of 2,4,4-trimethylpent-1-ene to 2,4,4-trimethylpentane, the tetrahydropyran complex of Re_2O_7 (D) and $ReO.2H_2O$ (G); for the reduction of maleic to succinic acid, *ex situ* rhenium black (A) and Re_2O_3 (C); for the reduction of the C=C double bond in the side chain of styrene to ethylbenzene, Re_2O_3 (C); for the reduction of cyclohexanone to cyclohexanol, $ReO.2H_2O$ (G); for the reduction of the N=N double bond in azobenzene to aniline, ReO_3 (F); for the reduction of the C=C double bond in cyclohexene to benzene and cyclohexane, ReO_3 (F); for the reduction of the C=C bond in the carbonyl group of crotonaldehyde to n-butanol, $ReO_2 . 2.5H_2O$ (E); for the reduction of butan-2-one to n-butanol, $ReO.2H_2O$ (G); for the reduction of ethyl benzoate to benzyl alcohol, *in situ* rhenium black (B); for the reduction of acetophenone to 1-phenylethanol, Re_2O_3 (C); for the reduction of ethyl acetate to ethanol, *in situ* rhenium black (B). The best catalyst for the reduction of the carbonyl group in acetic, octanoic, and dodecanoic acid to the corresponding alcohol is $ReO.2H_2O$ (G); for the reduction of hexanoic acid to n-decanol, *in situ* rhenium black (B); for the reduction of benzoic acid to toluene, $ReO.2H_2O$ (G); for the reduction of amino and nitro groups, and also hydrazobenzene to aniline, *ex situ* rhenium black (A). Conditions leading to the synthesis of various important alcohols from their corresponding acids have also been discovered[50] (see Table 1, No. 22-28).

From a comparison of the activity of rhenium catalysts with that of the conventional hydrogenation catalysts (Raney-Ni, PtO_2, and $CuCr_2O_4$), Broadbent concludes[50] that the rhenium catalysts are inferior to PtO_2 and Raney-Ni for the reduction of nitrobenzene to aniline, of styrene to ethylbenzene, and of cyclohexanone to cyclohexanol. However, the rhenium catalysts are unique in their ability to reduce acids to alcohols.

By using different catalysts based on rhenium oxide, other valuable products can be obtained. As Table 2 shows, Re_2O_3 reduced by sodium borohydride (C) can be used to reduce the C=C bond and the NO_2 group when chlorine or bromine atoms are present in the molecule (for example, *p*-chlorostyrene to *p*-chloroethylbenzene and *p*-bromonitrobenzene to *p*-bromoaniline); the tetrahydropyran complex of Re_2O_7, unlike other rhenium catalysts, allows the hydrogenation of the aromatic ring (see Table 2, compounds 6, 7, 9, 10). In the presence of $ReO_2 . 2.5H_2O$ (E) the olefin bond is reduced more rapidly than the carbonyl (14, 15) and the carboxyl group (16-18); ReO_3 (F) is an active catalyst for the reduction of various carboxylic acids (19-22) to the corresponding alcohols, and also of amides (28-30) to alkylamines. The ability of this catalyst selectively to reduce carboxyl groups without affecting the aromatic ring is also remarkable (26, 29, 30). It is evident from the examples given in Table 2 that the $ReO.2H_2O$ catalyst, prepared by reduction with alkali metals in ethylamine, is the most effective of the rhenium catalysts for the hydrogenation of carboxylic acids to alcohols (32-34), and for the reduction of nitro compounds to amines (39-42) and of ketones to alcohols (44-56).

Balandin and coworkers[56] obtained 100% yield in the hydrogenation of cyclohexene, octene, benzene, and acetone on a skeletal rhenium catalyst under a hydrogen

Table 1. Activity of rhenium catalysts towards the reduction of various organic compounds.

No.	Initial compound	Catalyst	Reaction conditions: solvent	t, °C	hydrogen pressure atm	time, h	Yield wt.%	Product
1	2	3	4	5	6	7	8	9
1	Hex-1-ene	B	none	100	156	2.5	100	n-Hexane
		C	none	68	220	7.0	100	
		B	none	154	200	2.0	100	
		F	none	95	205	15.0	100	
		G	none	119	200	2.5	100	
2	Hex-2-ene	C	none	110	239	4.0	100	n-Hexane
		D	none	122	245	3.0	100	
		G	none	151	200	3.0	100	
3	2,4,4-Trimethylpent-1-ene	C	none	140	252	2.5	100	2,4,4-Trimethylpentane
		D	none	91	218	3.0	100	
		G	none	200	200	0.5	100	
4	Maleic acid	A	Dioxan	148	177	2.5	100	Succinic acid
		B	none	196	286	12.0	91	
		C	Water	130	258	1.0	100	
		E	Petroleum ether	105	200	8.0	100	
5	Styrene	A	C_2H_5OH	108	156	3.5	100	Ethylbenzene
		B	C_2H_5OH	109	165	4.0	86	
		C	C_2H_5OH	25	194	6.0	100	
		C	C_2H_5OH	66	214	1.5	100	
		D	C_2H_5OH	107	255	2.0	100	
		E	C_2H_5OH	94	200	5.0	100	
		F	Cyclohexane	135	205	40.0	100	
6	Cyclohexanone	B	none	154	270	3.0	100	Cyclohexanol
		D	C_2H_5OH	113	248	5.0	100	
		E	none	115	200	12.0	100	
		G	none	119	200	2.5	100	
7	Azobenzene	B	none	125	249	24.0	92	Aniline
		F	none	195	205	15.0	96	
8	Cyclohexene	D	C_2H_5OH	151	264	13.0	100	Cyclohexane
		E	none	132	200	6.0	100	
		F	none	131	205	4.0	100	
		G	none	105	200	16.0	100	
9	Benzene	D	none	160	242	10.0	100	Cyclohexane
		E	none	177	200	14.0	100	
		F	none	240	205	4.0	100	
10	Crotonaldehyde	E	C_2H_5OH	148	200	8.0	100	n-Butanol
		F	Cyclohexane	147	205	16.0	100	
		G	C_2H_5OH	140	200	20.0	100	
11	Butan-2-one	E	none	100	200	4.0	100	Butan-2-ol
		C	none	72	217	3.0	100	
		G	none	100	200	2.5	100	
12	Ethyl benzoate	B	Cyclohexane	250	290	48.0	89	Benzyl alcohol
		F	ditto	237	205	80.0	93	
13	Acetophenone	A	C_2H_5OH	60	143	18.0	78	Methyl phenyl carbinol
		C	C_2H_5OH	150	255	1.0	100	
14	Ethyl acetate	B	none	148	191	11.0	100	Ethanol
		F	none	175	205	50.0	84	
15	Acetic acid	B	H_2O	150	168	10.0	100	Ethanol
		G	H_2O	145	200	4.5	100	
16	Octanoic acid	B	H_2O/dioxan	163	193	14.0	100	n-Octanol
		F	Cyclohexane	144	205	7.0	100	
		G	H_2O	173	200	5.0	100	
17	n-Decanoic acid	B	H_2O/dioxan	137	173	3.5	100	n-Decanol
		G	H_2O	173	200	6.0	100	
18	n-Dodecanoic acid	B	H_2O/dioxan	160	186	10	100	n-Dodecanol
		G	H_2O	177	200	7	100	
19	Benzoic acid	B	Benzene	254	190	15	91	Toluene
		G	H_2O	198	200	10	100	
20	Hydrazobenzene	B	Cyclohexane	185	280	42	97	Aniline
		F	ditto	185	205	33	100	
21	Nitrobenzene	A	C_2H_5OH	100	143	3	100	Aniline
		B	none	165	143	3	100	
		C	C_2H_5OH	75	195	4	100	
		F	none	226	205	25	100	
		G	none	106	200	7	100	
22	Trifluoroacetic acid	B	H_2O	207	300	18.5	100	Trifluoroethanol
23	Heptafluorooleic acid	B	H_2O	190	302	17	70	Heptafluorobutanol
24	Phenylacetic acid	B	none	149	160	14	78	2-Phenylethanol

Table 1 (contd.)

No.	Initial compound	Catalyst	Reaction conditions: solvent	t, °C	hydrogen pressure atm	time, h	Yield wt.%	Product
1	2	3	4	5	6	7	8	9
25	Lactic acid	B	none	150	258	8	84	Propylene glycol
26	Levulinic acid	B	none	106	150	18	71	β-Valeroacetone
27	β-Alanine	B	H_2O	250	210	32	92	Propanol
28	Glutaric acid	B	Dioxan	210	184	5	82	Pentane-1,5-diol
		B	H_2O	250	179	50	100	
29	*N*-Ethylacetamide	B	C_2H_5OH	245	352	22	96	*N,N*-Diethylaniline

pressure of 100–130 atm and temperature in the range 160–180°C. With this catalyst, the reduction of dimethyl maleate goes to completion even at room temperature and atmospheric pressure.

Platonov[46] was the first to note the interesting fact that rhenium catalysts can be activated by controlled amounts of typical catalyst poisons such as H_2S and As_2O_3. This effect was investigated in the particular case of ethanol dehydrogenation. At 500°, 30.7% of acetaldehyde and 0.9% of ethylene are formed from ethanol in the presence of a rhenium catalyst. On adding H_2S or As_2O_3 at a concentration of 0.004 mole per mole of ethanol the yields became (under otherwise identical conditions) 47.8 and 6.1% (with H_2S) and 43 and 3.8% (with As_2O_3) of aldehyde and ethylene respectively. With a further increase in the concentration of the poison to 0.008 mole per mole of alcohol, the yield of aldehyde falls off. Whereas formaldehyde is fully decomposed on a rhenium catalyst, the decomposition is suppressed[57] in the presence of H_2S or As_2O_3 (41.7 and 30.2% respectively of CH_2O are detected at 400°). The catalytic conversion of cyclohexanol yields mainly phenol[47], whereas in the presence of finely divided rhenium the main product is cyclohexanone. These observations led to an intensive study of the catalytic properties of rhenium sulphide.

The dehydrogenation of alcohols to aldehydes and ketones in the presence of rhenium sulphide was investigated by Platonov[58]. The products obtained from methanol, ethanol, and isopropanol (at 400, 550, and 500° respectively) contained 53.2, 53.5, and 91.4% of the appropriate aldehyde or ketone; cyclohexanol at 500° gave 78.8% of phenol and 6.7% of cyclohexanone. The interesting catalytic properties of rhenium sulphide are ascribed[58] to the similarity of its crystal lattice to that of MoS_2, which is extensively used as a catalyst for various reactions. Thus, formaldehyde, acetaldehyde, and acetone can be obtained in high yields from the corresponding alcohols by using ReS_2 as a catalyst.

The rhenium sulphides (ReS_2 and Re_2S_7) have been investigated by Broadbent and coworkers[59] as liquid-phase hydrogenation catalysts. The hydrogenations were carried out in a bomb containing 0.5 mole of the compound, a solvent, and 2.5 g of the catalyst per mole of the compound to be hydrogenated, under a pressure of hydrogen between 56 and 300 atm. The reaction conditions and the results obtained in the presence of rhenium heptasulphide and disulphide are listed in Table 3. The reductions obtained on Re_2S_7 include styrene to ethylbenzene, 1,1-methylphenylethanol (2-phenylpropan-2-ol) to cumene, maleic to

Table 2. Reduction of organic compounds in the presence of various rhenium catalysts with over 60% yield.

No.	Initial compound	Solvent	Temp., °C	Pressure atm	Reaction time, h	Yield, wt.%	Reaction product	Catalyst
1	*p*-Chlorostyrene	C_2H_5OH	34	197	11.0	100	*p*-Chloroethylbenzene	Re_2O_3 (C)
2	Pentan-3-one	C_2H_5OH	90	220	4.0	89	Pentan-3-ol	Re_2O_3 (C)
3	*p*-Bromonitrobenzene	C_2H_5OH	124	222	5.5	100	*p*-Bromoaniline	Re_2O_3 (C)
4	Capronitrile	none	240	306	7.0	69	Trihexylamine	Re_2O_7 (D)
5	Isobutyric acid	none	255	311	3.0	70	Isobutanol	Re_2O_7 (D)
6	Toluene	none	174	242	15.0	100	Methylcyclohexane	Re_2O_7 (D)
7	Cumene	none	148	255	11.0	71	Isopropylcyclohexane	Re_2O_7 (D)
8	t-Butylbenzene	none	195	272	9.0	100	t-Butylcyclohexane	Re_2O_7 (D)
9	*p*-Xylene	none	162	240	3.0	89	1,4-Dimethylcyclohexane	Re_2O_7 (D)
10	Phenol	Cyclohexane	170	260	15.0	92	Cyclohexanol	Re_2O_7 (D)
11	4-Nitrophenyl ether	none	160	240	3.0	100	4-Aminodiphenyl ether	Re_2O_7 (D)
12	Diphenylmethane	none	208	274	9.0	70	Cyclohexylphenylmethane	Re_2O_7 (D)
13	Acetophenone	none	143	200	8.0	64	1-Phenylethanol	$ReO_2 \cdot 2.5H_2O$ (E)
14	Hex-5-en-2-one	none	166	200	6.0	100	Hexan-2-ol	$ReO_2 \cdot 2.5H_2O$ (E)
15	2-Allylcyclohexanone	none	168	200	10.0	72	2-Propylcyclohexanone	$ReO_2 \cdot 2H_2O$ (E)
16	Crotonic acid	Petroleum ether	188	200	7.0	68	Butyl butyrate	$ReO_2 \cdot 2H_2O$ (E)
17	Vinylacetic acid	ditto	161	200	12.0	100	Butyric acid	$ReO_2 \cdot 2H_2O$ (E)
18	Levulinic acid	none	152	200	12.0	100	γ-Valerolactone	$ReO_2 \cdot 2H_2O$ (E)
19	Butyric acid	Cyclohexane	144	205	10.0	100	n-Butanol	ReO_3 (F)
20	Crotonic acid	H_2O	146	205	10.0	80	n-Butanol	ReO_3 (F)
21	Valeric acid	none	145	205	11.0	75	n-Pentanol	ReO_3 (F)
22	Undecylenic acid	H_2O	156	205	12.0	100	n-Undecanol	ReO_3 (F)
23	n-Butyl butyrate	none	218	205	28.0	100	n-Butanol	ReO_3 (F)
24	Pentan-3-one	none	161	205	1.0	100	Pentan-3-ol	ReO_3 (F)
25	Butan-2,3-diol	C_2H_5OH	204	205	10.0	73	Butan-2,3-diol	ReO_3 (F)
26	Benzaldehyde	Cyclohexane	124	205	20.0	88	Benzyl alcohol	ReO_3 (F)
27	Nitrocyclohexane	none	234	205	36.0	68	Cyclohexylamine	ReO_3 (F)
28	Acetamide	Cyclohexane	200	205	18.0	88	Ethylamine	ReO_3 (F)
29	Benzamide	C_2H_5OH	220	205	49.0	69	Benzylamine	ReO_3 (F)
30	Acetanilide	Cyclohexane	185	205	31.0	71	*N*-ethylaniline	ReO_3 (F)
31	Hex-5-en-2-one	C_2H_5OH	81	200	6.0	72	Hexan-2-one	$ReO \cdot 2H_2O$ * (G)
32	Propionic acid	H_2O	162	200	6.0	100	n-Propanol	ReO_3 (F)
33	Isobutyric acid	H_2O	172	200	5.0	95	Isobutanol	ReO_3 (F)
34	Valeric acid	H_2O	168	200		87	Pentanol	ReO_3 (F)
35	1-Phenylbut-2-ene	none	171	200	2.5	100	Butylbenzene	ReO_3 (F)
36	Pyridine	C_2H_5OH	205	200	7.0	100	Piperidine	ReO_3 (F)
37	Hex-5-en-2-one	C_2H_5OH	68	200	10.0	91	Hexan-2-one	$ReO \cdot 2H_2O$** (G)
38	2-Allylcyclohexanone	C_2H_5OH	125	200	6.0	73	2-Propylcyclohexanone	$ReO \cdot 2H_2O$* (G)
39	Nitrocyclohexane	C_2H_5OH	120	200	7.0	100	Cyclohexylamine	$ReO \cdot 2H_2O$ (G)
40	*m*-Nitroacetophenone	C_2H_5OH	110	200	24.0	100	*m*-Aminoacetophenone	$ReO \cdot 2H_2O$ (G)
41	*m*-Nitrostyrene	C_2H_5OH	118	200	1.0	100	*m*-Aminostyrene	$ReO \cdot 2H_2O$ (G)
42	*m*-Nitrobenzaldehyde	C_2H_5OH	124	200	10.0	100	*m*-Aminobenzaldehyde	$ReO \cdot 2H_2O$
43	Propynol	C_2H_5OH	142	200	2.5	77	n-Propanol	$ReO \cdot 2H_2O$
44	Acetone	—	78	200	10.0	100	Propan-2-ol	$ReO \cdot 2H_2O$ (G) ***
45	3-Methylbutan-2-one	—	198	200	7.0	100	3-Methylbutan-2-ol	$ReO \cdot 2H_2O$ (G)
46	Pentan-2-one	—	136	200	11.0	100	Pentan-2-ol	$ReO \cdot 2H_2O$ (G)
47	Pentan-3-one	—	160	200	6.0	100	Pentan-3-ol	$ReO \cdot 2H_2O$ (G)
48	4-Methylpentan-2-one	—	180	200	5.0	100	4-Methylpentan-2-ol	$ReO \cdot 2H_2O$ (G)
49	Hexan-2-one	—	135	200	11.5	100	Hexan-2-ol	$ReO \cdot 2H_2O$ (G)
50	Hexan-2,5-dione	—	121	200	10.5	95	Hexan-2,5-diol	$ReO \cdot 2H_2O$ (G)
51	Heptan-2-one	—	172	200	3.5	96	Heptan-2-ol	$ReO \cdot 2H_2O$ (G)
52	Heptan-3-one	—	152	200	5.0	100	Heptan-3-ol	$ReO \cdot 2H_2O$ (G)
53	Heptan-4-one	—	186	200	2.0	98	Heptan-4-ol	$ReO \cdot 2H_2O$ (G)
54	Cycloheptanone	—	175	200	8.5	100	Cycloheptanol	$ReO \cdot 2H_2O$ (G)
55	Octan-2-one	—	130	200	6.0	86	Octan-2-ol	$ReO \cdot 2H_2O$ (G)
56	Nonan-2-one	—	178	200	6.0	100	Nonan-2-ol	$ReO \cdot 2H_2O$ (G)

* Reduced by lithium ethylamide
** Reduced by lithium in liquid ammonia
*** Reduced by sodium in liquid ammonia

succinic acid, nitrobenzene to aniline, *p*-bromonitrobenzene to *p*-bromoaniline, allyl phenyl sulphide to propyl phenyl sulphide, diphenyl disulphide to thiophenol. The carbonyl double bond (acetophenone) is reduced less readily than the carbon–carbon double bond (styrene). The C–S bond is not broken during the hydrogenation of organosulphur compounds. Thus, allyl phenyl sulphide gives only propyl phenyl sulphide, diphenyl disulphide gives only thiophenol, thiophen gives only thiophane. If the reaction is carried out under more drastic conditions, for example at 300°, cyclohexane and benzene are formed from the thiophenol, and benzene is formed from the diphenyl disulphide. The nitro group is readily reduced at or just above room temperature. Rhenium disulphide is less active than the heptasulphide. The activity of rhenium sulphide catalysts towards a number of reactions was compared with the activity of the existing catalysts molybdenum sulphide and cobalt sulphide[59]. The most active hydrogenation catalyst was found to be Re_2S_7, followed by ReS_2, MoS_2, and CoS_x (in that order). Cobalt polysulphide has a high activity (comparable to that of Re_2S_7) only in the reduction of nitrobenzene to aniline.

Thus, Re_2S_7 has been shown to be an active liquid-phase hydrogenation catalyst. It induces quantitative reduction of styrene, cyclohexene, maleic acid, nitrobenzene, *p*-bromonitrobenzene, and diphenyl sulphide.

Balandin and coworkers[60] studied the catalytic reduction of chloronitrobenzenes in the presence of Re_2S_7 (in amounts between 2 and 10% of the weight of chloronitrobenzene) at 100–123° and for reaction times of 40–60 h. *p*-Chloronitrobenzene, 3,4-dichloronitrobenzene, and 2,4,5-trichloronitrobenzene gave the corresponding chloroanilines in 100% yield (measured chromatographically).

The catalytic reduction of functional groups in sulphur compounds is difficult to realise, because all known catalysts are susceptible to catalytic poisoning (to a greater

or lesser extent) by sulphur in the bivalent state. However, Re_2S_7 proved to be very active even under these conditions[61].

Aretos and Viall[62] reduced 2-nitrothiophen to 2-acetylaminothiophen at 100° in the presence of acetic anhydride:

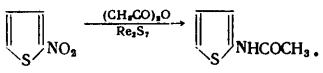


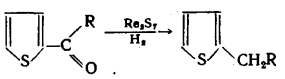
Table 3. Hydrogenation in the presence of sulphide catalysts.

Initial compound	Amount of catalyst, g/mole of initial cpd.	Solvent	Pressure, atm	Temperature, °C	Time, h	Reduction product	Yield, %
			Re_2S_7 catalyst				
Styrene	2.5	C_2H_5OH	120	100-135	1	Ethylbenzene	100
Phenylacetylene	2.5	C_2H_5OH	133	106-135	1.75	Ethylbenzene	70
2-Phenylpropan-2-ol	2.5	C_2H_5OH	140	130	0.33	Cumene	100
Cyclohexene	0.5	C_2H_5OH	140	240	3	Cyclohexane	92
Maleic acid	1.0	H_2O	91	150	5	Succinic acid	100
Acetophenone	2.5	C_2H_5OH	160	216-230	0.17	Ethylbenzene	85
Nitrobenzene	2.5	C_2H_5OH	133	25	6	Aniline	100
Nitrobenzene	2.5	C_2H_5OH	133	60-100	0.5	Aniline	100
p-Bromonitrobenzene	2.5	Methyl cellosolve	133	60	0.5	*p*-Bromoaniline	100
Bromobenzene	2.5	ditto	190	225-250	3	Bromobenzene	89
						Benzene	11
Pentyl phenyl sulphide	2.5	C_2H_5OH	133	150-160	0.5	Propyl phenyl sulphide	100
Diphenyl sulphide	2.5	none	160	280-300	2	Benzene	94
Diphenyl disulphide	2.5	Methyl cellosolve	154	165-195	1	Thiophenol	100
Thiophen	2.5	none	140	230-260	3.75	Thiophane	70
						Butanthiol	0
			ReS_2 catalyst				
Styrene	1.0	C_2H_5OH	140	150-180	1	Ethylbenzene	63
Nitrobenzene	0.5	C_2H_5OH	125	110-200	2	Aniline	94
Allyl phenyl sulphide	2.5	C_2H_5OH	160	240-245	1	*p*-Propyl phenyl sulphide	91

The thiophen ring was hydrogenated at 200°, giving thiophane and 2-methylthiophane. Various 1,2-dithiol-3-thionones have also been hydrogenated at 180-200°:

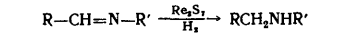
where R = 4-C_6H_5, 5-C_6H_5, and 5-*p*-$CH_3OC_6H_4$. In every case, ring opening was observed, with formation of benzene and a thiol.

Ryashentseva and coworkers[63,64] achieved selective reduction of the carbonyl group in a series of thiophen compounds. In the presence of rhenium heptasulphide, they obtained 2-methylthiophen and 2-ethylthiophen (in 50 and 80% yield respectively) from 2-thiophenal and 2-acetothienone in dioxan under autoclave conditions (170-190°, 100-130 atm hydrogen pressure):

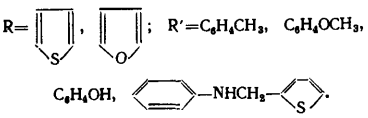


where R = H, CH_3.

The same workers[65,66] also found conditions leading to the selective hydrogenation of the azomethine group (-C=N-) without attacking the thiophen or aromatic ring. Thus, they prepared the appropriate secondary amines from *N*-thienylidene-*p*-toluidine, *N*-thienylidene-*p*-anisidine, *N*-thienylidene-*p*-aminophenol, *N*-furfurylidene-*p*-toluidine, and *N,N'*-dithienylidene-*p*-phenylenediamine:

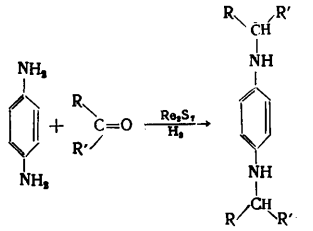


where

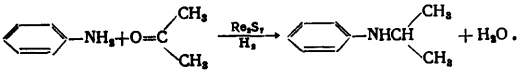


Conditions for the reduction of azomethines to secondary amines in the presence of 100 mg Re_2S_7 in dioxan, and under a hydrogen pressure of 130 atm, are summarised in Table 4. It is evident that the presence of *p*-toluidine, *p*-anisidine, or *p*-aminophenol groups has practically no effect on the selectivity of the hydrogenation of the azomethine group: reduction takes place at 150-170° in 3 h in the presence of 1.5-2 g Re_2S_7 per mole of the azomethine. If the thiophen residue is replaced by furan in the original azomethine, the hydrogenation (under otherwise comparable conditions) is hindered, and the yield of secondary amines drops to ~40%. It has been shown that the catalyst can be re-used a number of times.

Ryashentseva and coworkers[67,68] studied the alkylation of *p*-phenylenediamine and its hydroquinone complex by ketones (acetone, ethyl methyl ketone, and cyclohexanone) in the presence of Re_2S_7. Reaction took place, in a rotating autoclave, at 150-200° and under 100-130 atm hydrogen pressure, in 2.5-3 h. *N,N'*-di-isopropyl-, *N,N'*-di-isobutyl-, and *N,N'*-dicyclohexyl-*p*-phenylenediamine were obtained in 60-94% yield, as well as their hydroquinone complexes. The best results were obtained by using a three-fold excess of the ketone. Alkylation takes place by the scheme



Dovell and Greenfield[69] used rhenium heptasulphide for the reductive alkylation of aniline by acetone to give *N*-isopropylaniline:



The alkylation took place in an autoclave at 140° and 80-100 atm hydrogen pressure. After 4.4 h, *N*-isopropylaniline was obtained in 90% yield (measured by gas-liquid chromatography).

These results show that the reductive alkylation of aromatic amines in the presence of rhenium heptasulphide is not accompanied by hydrogenation of the benzene ring, cleavage of the C=N bond, or reduction of the ketone. Rhenium heptasulphide was the most active of all the sulphide catalysts examined[68,69] in this particular reaction.

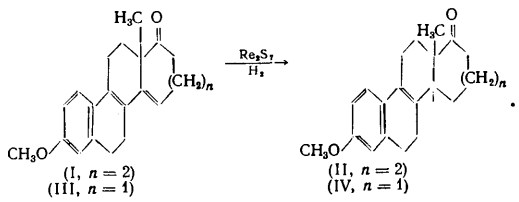
Platonova and coworkers[70] were able to reduce the double bond in a series of steroid compounds in the presence of Re_2S_7. Thus, they isolated in ~15% yield the methyl ether of *d,l-D*-homo-$\Delta^{1,3,5,8(8)}$-oestrapentaene-one-17a (II), with a *cis* configuration of the *C* and *D* rings, from the methyl ether of *d,l-D*-homo-$\Delta^{1,3,5(10),8,14}$-oestrapentaenone-17a (I) in benzene and under hydrogen pressure.

Table 4.

Initial compound, g	Reaction temp., °C	Yield of products, %	
		secondary amine	primary amine
N-thienylidene-*p*-toluidine (Ref.10)	170[a]	55	10
	170[b]	60	10
N-thienylidene-*p*-anisidine (Ref.10)	150	55	10
	200	20	60
N-thienylidene-*p*-aminophenol (Ref.5)	150	60	
N-furfurylidene-*p*-toluidine (Ref.10)	150	39	10
	150[c]	40	12
	150[d]	40	13
	150[e]	25	14
	150[f]	29	14
N,N'-dithienylidene-*p*-phenylene-diamine (Ref.5)	170	22	

[a] Pressure 125 atm; [b] Pressure 170 atm; [c] Re_2S_7 150 mg; [d] Re_2S_7 200 mg; [e] in benzene; [f] in n-hexane.

In a similar way, the methyl ether of $\Delta^{1,3,5(10),8}$-oestratetraenone-17 (IV) was obtained in 40% yield from the methyl ether of $\Delta^{1,3,5(10),8,14}$-oestrapentaenone-17 (III). Products of the partial and the complete reduction of the keto group in position 17 were isolated and identified among the side-products:



(I, $n = 2$) (III, $n = 1$) (II, $n = 2$) (IV, $n = 1$)

Broadbent and Whittle[71] showed that Re_2Se_7 can also be a good hydrogenation catalyst at 100–240° and 200–300 atm pressure, with or without a solvent. Hydrogenation conditions and yields (which sometimes exceed 70%) are listed in Table 5.

It is evident from Table 5 that the C=O bond is saturated more readily than the C=C bond in the presence of Re_2Se_7, unless the latter is associated with other double bonds. Hydrogenation of the C=C bond in thiophen and in allyl phenyl sulphide proceeds without rupture of the C–S bond. By studying the reduction of *p*-bromonitrobenzene it was shown that the carbon–halogen bond is also unattacked whilst the nitro group is easily reduced. The benzene ring is fairly resistant to hydrogenation: only 4.5% of cyclohexane is formed from benzene.

Table 5. Hydrogenation in the presence of Re_2Se_7.

Initial compound	Solvent	Pressure atm	Temp., °C	time, h	Hydrogenation product	Yield, %
Nitrobenzene	C_2H_5OH	240	155	1.25	Aniline	100
Nitrobenzene	none	240	150	4.0	Aniline	100
Sodium *p*-nitrophenate	H_2O	226	130	1.0	*p*-Aminophenol	100
Nitropropane	C_2H_5OH	242	115	3.0	Propylamine	100
2,4,4-Trimethylpent-1-ene	none	287	200	5.0	Iso-octane	93.5
Cyclohexene	C_2H_5OH	306	200	3.0	Cyclohexane	40.0
Styrene	C_2H_5OH	246	135	2.0	Ethylbenzene	94.0
Crotonic acid	none	262	150	8.0	Butyric acid	100.0
Maleic acid	H_2O	207	60	7.0	Succinic acid	100.0
Maleic acid	Dioxan	265	150	0.75	Succinic acid	100.0
Cinnamic acid	Dioxan	260	145	2.5	Hydrocinnamic acid	100.0
Pentyl phenyl sulphide	C_2H_5OH	292	195	2.0	*p*-Propyl phenyl sulphide	100.0
Phenylacetylene	C_2H_5OH	268	100	1.0	Ethylbenzene	73.6
					Polymer	25.4
Thiophen	none	322	250	13.0	Thiophane	100.0
Butanone	none	238	105	5.0	Butan-2-ol	100
Cyclohexanone	C_2H_5OH	266	155	9.0	Cyclohexanol	100
Acetophenone	C_2H_5OH	248	150	2.25	Ethylbenzene	88
					1-Phenylethanol	10
p-Nitrobromobenzene	C_2H_5OH	235	100	3.0	*p*-Bromoaniline	100
2-Phenylpropan-2-ol	C_2H_5OH	264	160	1.1	Cumene	100
Benzyl phenyl sulphide	C_2H_5OH	326	190	7.0	Benzene	100
					Toluenethiol	100

Comparing the activity of Re_2Se_7 towards hydrogenation reactions with the activity of rhenium, molybdenum, and cobalt sulphides we find[59] that Re_2Se_7 is second only to Re_2S_7, but is much more active than molybdenum and cobalt sulphides. In the reduction of nitrobenzene it was shown that the Re_2Se_7 catalyst is unaffected by nitrogen, phosphorus, sulphur, selenium, and tellurium compounds, but is sensitive to arsenic compounds.

III. SUPPORTED RHENIUM CATALYSTS (dehydrogenation of alcohols, rearrangement of hydrocarbons, and treatment of petroleum fractions)

Platonov and coworkers[41,48] prepared a rhenium catalyst on a ceramic carrier containing a large proportion of alumina by a modified "nitric acid" method. The catalyst was shown to have a high selectivity towards the dehydrogenation of ethanol to acetaldehyde. However, the yield of acetaldehyde was only 14% at 600°.

In Balandin's laboratory, rhenium catalysts were prepared[72] by impregnating the carrier (active carbon, alumina, asbestos, or quartz) with solutions of ammonium perrhenate or of the rhenium–dioxan complex ($Re_2O_7.C_4H_8O_2$).[73] The highest activity was found in the rhenium catalysts supported on carbon, prepared by the dioxan method[72,74]. Transformations of primary and secondary alcohols (ethanol, n-propanol, isopropanol, and s-butanol) were investigated. Isopropanol at 150–200° gave acetone with a yield approaching the maximum thermodynamically possible value. The dehydrogenation of primary alcohols is complicated by the formation of esters and by decarbonylation of the resulting aldehyde. The intermediate product in the formation of γ-butyrolactone from 1,4-butandiol is γ-hydroxyoleic aldehyde.

Balandin, on the basis of the structural correspondence principle of the multiplet theory of catalysis, was the first to suggest the possibility of dehydrogenation of six-membered rings by a sextet mechanism on rhenium, since the latter has hexagonal symmetry.

Balandin and coworkers[75] studied the dehydrogenation kinetics of cyclohexane, methylcyclohexane, and ethylcyclohexane on rhenium catalysts supported on carbon. The rate of dehydrogenation decreases with increase of molecular weight of the hydrocarbon. The same workers[75] investigated the dependence of catalyst activity and activation energy for the dehydrogenation of cyclohexane upon the rhenium content of the catalyst. An activation energy of 12.8 kcal mole^{-1} was found to correspond to a rhenium content of 30 wt.% in the catalyst. It was also shown that the relative benzene adsorption coefficient is independent of the reaction temperature. The dehydrogenation of cyclohexane on rhenium is a zero-order reaction. The carbon-supported rhenium catalyst develops its highest activity during the first few minutes of the reaction[76]. Thus, the yield of benzene from cyclohexane at 360–380° is 90–95% after the first 5–7 min. Subsequently, the activity falls to a constant value at some intermediate level. The catalyst is regenerated by hydrogen treatment at 500° for 1–1.5 h. The authors[76,77] offer an explanation of the effect of the carrier on the activity of the catalyst in this reaction. They suggest that rhenium on carbon is similar to platinum on carbon, and should be an active dehydrogenation catalyst for cyclohexane under conditions of energy correspondence: this prediction is confirmed by experiment. However, their explanation of the results obtained with rhenium–alumina catalysts is less convincing, and is inconsistent with other experimental results[78–81]. Thus, according to Balandin, the ratio of M–M to O–O interatomic distance is: for Pt, 2.77/2.64 = 1.05; for Re, 2.736/2.64 = 1.035; for Ni, 2.48/2.64 = 0.94. The corresponding deviations from the integral value of 1 are: +5% for Pt, +3.5% for Re, and –6.4% for Ni. They conclude that negative deviations are favourable, and therefore that Ni on Al_2O_3 should be the most active catalyst. With rhenium the correspondence between interatomic distances is fairly good, but the deviation (though small) is positive, and therefore the rhenium lattice is under compression and the catalytic activity is low (the yield of benzene from cyclohexane is 5–7% with a Re/Al_2O_3 catalyst). But according to this argument the activity of the platinum–alumina catalyst (the industrial platinum forming catalyst) should be negligible. The authors ascribe the activity of this catalyst to the state of the platinum. They postulate relatively large Pt crystals, insensitive to the influence of the carrier, even though platinum forming catalysts are known to contain only 0.3–0.5% of platinum on alumina.

Balandin and coworkers[76] also studied the dehydrocyclisation of n-heptane on a rhenium–carbon catalyst. At 468°, and with a flow of n-heptane of 0.173 ml min^{-1}, the product contains 14.0% of aromatic hydrocarbons and 9.4% of unsaturated compounds. Later they examined the properties of a rhenium–carbon catalyst made by the dioxan method[56] and containing 30% of rhenium. On this catalyst, complete reduction of cyclohexene to cyclohexane and of acetone to isopropanol was obtained in 1–2 h at 160–180° and 70–110 atm hydrogen pressure; cinnamic aldehyde was quantitatively reduced to hydrocinnamic alcohol at 250° and 110–130 atm pressure.

It was also shown[82] that the rate of dehydrogenation of cyclohexane on a rhenium–carbon catalyst is higher than the rate of dehydrogenation of cyclohexene, and therefore that cyclohexene cannot be an intermediate in the transformation of cyclohexane to benzene.

Isagulyants and coworkers[83] studied the mechanism of conversion of cyclohexane and of cyclohexene at 270–400° at atmospheric pressure in the presence of the same catalyst. They showed that cyclohexene is not a precursor in the formation of benzene from cyclohexane: benzene is formed directly from cyclohexane. This conclusion is consistent with the earlier observations[82] from the same laboratory.

Ryashentseva and Minachev[84–88] studied the properties of rhenium catalysts with special reference to the reactions of C_5–C_7 hydrocarbons under reforming conditions.

Metals in the neighbouring groups of the Periodic Table (VI and VIII) have been studied intensively from this point of view, and some of them have found application in various industrial processes (in particular, petroleum refining).

The reactions of hydrocarbons have been used to study the properties of rhenium catalysts as a function of metal content, nature of the carrier, specific surface area, catalyst treatment, and reaction conditions. The experiments were made in a flow reactor under pressure of hydrogen. The products of catalysis were analysed by gas–liquid chromatography. Ryashentseva and Afanas'eva[84] developed a procedure for extracting the rhenium from rhenium–alumina and rhenium sulphide–alumina catalysts, using 5% HNO_3 and HNO_3–H_2O_2 mixtures respectively, followed by a photometric determination.

Catalysts containing 20% of rhenium were found to be the most active of the rhenium–alumina catalysts[79]. At 380°, 5 atm hydrogen pressure, and a feed rate of 1.0 h^{-1} [litre h^{-1}? (Ed. of Translation)] (5 : 1 ratio of hydrogen to hydrocarbon), up to 80% of benzene was obtained from cyclohexane during the first few hours' operation, but the activity of the catalyst decreased with time, and after 21 h the product contained only 5% of benzene. Methylcyclopentane and n-hexane under the same conditions undergo mainly hydrogen cracking. Convincing results were obtained with a catalyst containing 5% of rhenium on zeolite. In this system, high selectivity for the cyclohexane dehydrogenation reaction is observed.

Treatment of the rhenium–alumina catalysts with hydrogen sulphide[85] increases their activity. As in the case of the rhenium–alumina catalysts themselves, the activity increases with rhenium content. For example, for catalysts treated with hydrogen sulphide and containing 1, 5, 10, 15, and 20% of rhenium the yield of benzene from cyclohexane is 2.9, 20, 31, 34, and 76% respectively. The catalyst containing 20% of rhenium is the most active. At 500°, 5 atm hydrogen pressure, and 5 : 1 hydrogen to hydrocarbon ratio, this catalyst gives up to 80% of benzene from cyclohexane, and 53% of benzene from methylcyclopentane. Under the same conditions, n-hexane suffers appreciable cracking, but the product contains 10% of aromatic hydrocarbons, indicating some measure of dehydrocyclisation.

Prinzler and Klotzsche[89] studied the dehydrogenation of cyclohexane to benzene, the dehydrocyclisation of n-heptane to toluene, the isomerisation of n-pentane to isopentane, and the demethylation of toluene to benzene on $Re–Al_2O_3$ and $Re–Al_2O_3.SiO_2$ catalysts at atmospheric pressure and 480–490°. They showed that in these reactions the rhenium catalysts are much less active than the platinum–alumina catalysts. At feed rates of 0.5–5.0 changes per hour, 5% of benzene is formed from cyclohexane and only 1.7% of toluene from n-heptane. Addition of ZnO_2 to these catalysts does not raise their activity.

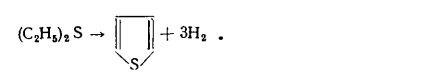
Müller and Wencke[90] studied the effect of different carriers on the catalytic properties of rhenium catalysts. They examined two modifications of alumina (α and γ) and beech charcoal. The chosen model reaction was the gas-phase dehydrogenation of cyclohexane between 250 and 420° at ~50% conversion. Rhenium on α-Al_2O_3 had the

highest catalytic activity. Rhenium deposited on γ-Al_2O_3 shows the same activity only at much higher concentrations of the metal. The authors conclude that α-Al_2O_3 is a better carrier than γ-Al_2O_3 at low concentrations of rhenium; beech charcoal occupies an intermediate position.

Müller and Wencke offer the following explanation of their findings. The pure carriers have different BET surfaces: 939, 143, and 8 $m^2 g^{-1}$ for beech charcoal, γ-Al_2O_3, and α-Al_2O_3 respectively. Since α-Al_2O_3 has the smallest surface, catalytically active groupings of atoms can form on it at quite low metal concentrations (~0.5%). γ-Al_2O_3 requires a higher metal concentration to achieve the same condition. Beech charcoal, which has the largest surface area, should become catalytically active at significantly higher concentrations of the metal than is found in practice. The discrepancy is ascribed to the possibility of epitaxial growth, on the assumption that surface formations on the charcoal can lead to dehydrogenation of cyclohexane as well as the octahedral surface of the rhenium lattice.

Blackham and coworkers[91] studied the properties of rhenium–alumina catalysts as a function of the method of preparation of the catalyst in the dehydrocyclisation of n-heptane at 550–600° under atmospheric pressure. Rhenium catalysts are inferior to platinum catalysts in this reaction. Thus, up to 80% of dehydrocyclisation products are obtained with a 1% Pt–Al_2O_3 catalyst under optimum conditions, as compared with ~60% on a 5% Re–Al_2O_3 catalyst. Rhenium–alumina catalysts prepared by different methods had comparable activities.

Rhenium catalysts have been investigated[92] in the dehydrocyclisation of diethyl sulphide to sulphide to thiophen under 3 atm hydrogen pressure, apparent contact time 0.6 s, catalyst particle size 1–1.5 mm, and 15 wt.% concentration of the sulphide in helium:



The activity of rhenium catalysts in this reaction was found to be similar to that of other dehydrocyclisation catalysts, such as chromium and molybdenum. In the presence of rhenium, the dehydrocyclisation reaction is complicated by decomposition of the sulphide at the C–S bond, and the yield of thiophen is no more than 13% of the initial diethyl sulphide.

Sokolova and coworkers[60] obtained the appropriate chloroanilines in 100% yield from *p*-dichlorobenzene and trichlorobenzene in the presence of a 5% Re_2S_7–SiO_2 catalyst at 120–140° and 40–65 h reaction time.

The use of rhenium catalysts in the treatment of petroleum fractions at high temperatures in the presence of a pressure of hydrogen has been investigated[80,81,93].

A Patent by Hummel[80] discloses that the fraction boiling at 100–180°, containing 14% of aromatic hydrocarbons and having an octane number of 53, can be dehydrogenated at 475–500° under 50 atm pressure to give a 49% content of aromatics and an octane number of 71. The catalyst was prepared from a rhenium salt solution containing 3 g $litre^{-1}$ of rhenium, deposited on activated alumina to which 0.3% of fluoride and 0.1% of MgO had been added. Before the reaction, the catalyst was activated by hydrogen reduction at 475°. The preparative details of the catalyst are not disclosed in the Patent. It is shown[80] that the rhenium catalyst leads to isomerisation as well as to the formation of aromatic hydrocarbons from n-alkanes, and is more effective than platinum catalysts in this respect.

The same author[81] subsequently proposed the rhenium–alumina–silica catalyst for the production of liquid fuels from high-boiling hydrocarbon oils, jellies, and petroleum products under 100–700 atm pressure and at temperatures between 300 and 450°.

Lüder and Drescher[93] studied the application of rhenium catalysts in hydrogenation and reforming processes. The experiments were made with a fraction containing 13.6% of aromatic hydrocarbons, 43.5% of naphthenes, and 42.9% of alkanes. Rhenium catalysts on alumina were inferior to the industrial molybdenum and platinum catalysts, which gave 54% of aromatic hydrocarbons from the experimental fraction as compared with only 22% using the rhenium–alumina catalyst. Replacement of the NH_4ReO_4 by $KReO_4$ did not improve the aromatising properties of the catalyst. The authors succeeded in raising the content of aromatics to 32–36% and the octane number to 72–74 by using much higher proportions of rhenium in the catalyst and by including small amounts of MgO and fluorides.

Additions of iron had no effect, even in the presence of large amounts of rhenium. By varying the preparative conditions of the catalyst, up to 50% of aromatic hydrocarbons can be obtained in the reforming products, but the overall yield of liquid products is significantly decreased by the formation of gaseous hydrocarbons. However, a rhenium dehydrogenation catalyst for hydrocarbons boiling in the benzine range could not be prepared. Good results were obtained by treating a middle prehydrogenation oil with a rhenium catalyst supported on Fuller's earth. The rhenium content was 3 g $litre^{-1}$, corresponding to 0.4–0.5 wt.% (as compared with 5–10 wt.% in the hydrogenation media used in industrial catalysts). The rhenium was used as the metal or the sulphide. The authors[93] observed extensive fission of the oils: the yield of the fraction boiling up to 200° was 82%. Better results were obtained with a catalyst of composition 3 g $litre^{-1}$ supported on Fuller's earth treated with fluorides. The octane number of the reforming products obtained with an industrial catalyst was 60.1, whereas the rhenium catalyst gave a higher value (74.8). The catalyst was tested during 1150 h. A Diesel fraction gave a reforming product with cetane rating 45 and 47. However, the high initial activity of the rhenium catalysts falls off quite rapidly. If this shortcoming could be overcome, the rhenium catalyst would offer interesting possibilities for the treatment of middle oil fractions. The authors believe that rhenium catalysts will find industrial applications, but that more research is needed into their regeneration and into more general applications.

Minachevich and Ryashentseva[87] showed that between 32 and 47% of aromatic hydrocarbons can be obtained from the direct-distillation benzine fraction of b.p. 38.5–196°, containing 10% of aromatic hydrocarbons, by reforming with a 20% Re–Al_2O_3 catalyst (treated with hydrogen sulphide) at 480–490°, 5 atm pressure, flow rate 1.0 changes per hour, and 5 : 1 ratio of H_2 to hydrocarbons. The octane number (without tetraethyllead) increases from 47.8 to 71 and 87.2. Reforming of the benzine fraction (b.p. 89.5–126°) from the Volga–Urals region[87] increased the content of aromatics from 6 to 20–60%, and lowered the content of sulphur compounds from 0.017 to 0.002–0.007%. This catalyst was studied during 500 h, including 5 regenerations. Although the aromatising power of the catalyst was effectively restored after each regeneration, the stability gradually deteriorated. The yield of aromatic hydrocarbons during the first 30 h was 55–60%; subsequently the activity began to fall off, and after 60 h operation the content of aromatics was only ~20%. This level

of activity was retained for approximately 100 h, but after this period the activity decreased and the content of aromatic hydrocarbons fell to 12%.

Hence, the rhenium catalysts cannot compete with the industrial platinum catalysts as regards stability. Furthermore, their rhenium content must be much higher than the platinum content of conventional platinum forming catalysts.

IV. MIXED RHENIUM CATALYSTS (liquid-phase hydrogenation, rearrangement of hydrocarbons, and reforming of light petroleum fractions)

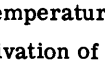
Sokol'skii and coworkers[94-99] studied the effect of adding rhenium on the activity and selectivity of various nickel catalysts for liquid-phase hydrogenation.

They investigated the hydrogenation of unsaturated compounds containing ethylene, acetylene, and aldehyde bonds, on nickel–silica catalysts, and showed[94] that the rate of hydrogenation is increased by adding up to 5% of rhenium to the catalyst. Higher rhenium contents degrade the activity of the catalyst. Very small additions of rhenium (<0.5%) were also found to deactivate the catalyst. By adding an alcoholic solution of potassium perrhenate to a Raney nickel catalyst, they were able to hydrogenate tetramethylbutynediol, vinyl ether, cinnamaldehyde, and vinylethynyldimethyl carbinol (2-methylhex-3-yne-5-ene-2-ol) in the liquid phase and to demonstrate the promoting action of potassium perrhenate. Addition of rhenium to the catalyst not only increases the rate of hydrogenation of unsaturated compounds, but also extends the useful life of the catalyst. For example, a nickel catalyst without rhenium can be used three times for liquid-phase hydrogenation, but it remains active during five operations if promoted with rhenium.

Hydrogenation of cotton-seed oil[95] on a Raney nickel–rhenium catalyst in absolute ethanol is 1.5–1.7 times faster than on a straight Raney nickel catalyst.

It was also shown[96,97] that the addition of 1–3% of rhenium to a nickel–aluminium alloy increases its activity towards the hydrogenation of cinnamic alcohol to phenylpropanol. If the rhenium content is increased to 5–7% the catalytic activity decreases, but in every case the rhenium-containing catalysts were more active than the nickel–aluminium alloy. The hydrogenation rate constant on a catalyst made from a 3% Re, 47% Ni, and 50% Al alloy was higher by a factor of 1.6 at 40° and a factor of 2 at 20° than the rate constant found in the hydrogenation of cinnamic alcohol on Raney nickel.

Rhenium–palladium alloy catalysts[98] have been studied in the hydrogenation of dimethylethynyl carbinol in water, 96% ethanol, 0.1*N* KOH in water and in ethanol, at 10, 20, 30, and 40°. Hydrogenation in water is produced by adsorbed hydrogen, but in ethanol the reaction involves hydrogen supplied from the bulk of the catalyst. The catalysts are stable both in aqueous and in alcoholic media, and show some selectivity when 0.1*N* KOH in 96% ethanol is used as the solvent. The reaction stops at the stage of half-hydrogenation. However, the palladium–rhenium catalyst is less active than the palladium–iridium alloy catalyst. The state of the surface during the reaction was monitored by potential measurements[99].

The activity of skeletal nickel–rhenium catalysts prepared from Ni–Re–Al alloys has been studied[100] in the hydrogenation of potassium maleate, potassium *o*-nitrophenate, and dimethylethynyl carbinol in 0.1*N* KOH solution, and of nitrobenzene in 50% ethanol. At temperatures below 40°, the skeletal nickel catalyst is deactivated towards the hydrogenation of compounds with multiple carbon–carbon bonds. At higher temperatures the rate of hydrogenation goes through a maximum as a function of rhenium concentration in the alloy. When potassium *o*-nitrophenate is reduced in 0.1*N* KOH, the reaction is drastically retarded as the rhenium content is increased, particularly at high temperatures. The rhenium was shown to increase the lattice parameter of the Raney nickel catalyst. The authors consider that the promoting effect of rhenium at elevated temperatures resides in its favourable influence on the activation of the  and –C≡C– bonds, and they ascribe the poisoning of the catalyst during the reduction of nitro compounds in alkaline media to oxidation of the rhenium or its hydride.

Mashkina and Vakurova[92] also demonstrated the promoting effect of rhenium. By adding 2.5% of rhenium to an industrial nickel–chromium catalyst, they obtained a much higher rate of hydrogenation (at 20° and under atmospheric pressure) of sulpholene to sulpholane:

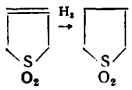


Table 6. Catalytic conversion of hydrocarbons on rhenium–palladium–alumina catalysts*.

Initial hydrocarbons	Contents in product wt.%						
	iso-C_6H_4						
	№ 1	№ 2	№ 1	№ 2	№ 1	№ 2	
	—	—	67.0	87.0			
	—	—	23.0	61.2			
n-C_6H_{14}	32.0	52.0					
	—	—					90

* No.1, 1% Pd, 1% Re, 98% Al_2O_3; No.2, 1% Pd, 1% Re, 98% Al_2O_3; H_2S: temperature 480°; pressure 10 atm; flow rate $v = 1.0\ h^{-1}$; H_2 to hydrocarbon ratio 5:1.

Ryashentseva and coworkers[101-104] studied the properties of mixed rhenium–palladium–alumina–silica catalysts towards the transformations of cyclohexane, methylcyclohexane, methylcyclopentane, and n-hexane[101,102]. The rhenium–palladium–alumina catalyst containing 1% of rhenium and 1% of palladium on fluorinated (0.4% F) alumina, and treated with hydrogen sulphide[102], was found to be the most active and stable towards the dehydrogenation of cyclohexane and methylcyclohexane, the dehydroisomerisation of methylcyclopentane, and the isomerisation of n-hexane. The results are summarised in Table 6. This catalyst was also used under reforming conditions on Baku B-70 light

petroleum and on the light petroleum fraction from the Volga-Urals oilfields. The results of these tests are given in Table 7.

Table 7. Properties of initial light petroleum fractions and of reforming products (470°, 10 atm, $v = 1.0\ h^{-1}$, H_2 : hydrocarbon = 5 : 1).

Properties	Initial fraction		Properties of product after 25 h operation of the catalyst		
			No.2 catalyst 1% Pd, 1% Re, Al_2O_3, H_2S		No.3 catalyst 1% Pd, Al_2O_3, H_2S
	Baku B-70	86–119°	B-70	86–119°	B-70
Refractive index n_D^{20}	1.4180	1.4040	1.4520	1.4260	1.4255
Specific gravity d_4^{20}	0.7529	0.7152	0.7928	0.7502	0.7545
Concentration of aromatic hydrocarbons, vol.%	5.5	6.0	57.0	38.0	20.5
Concentration of sulphur compounds, wt.%	0.0123	0.0116	0.009	0.010	0.008
	Engler distillation, °C				
Boiling begins	67.0	86.0	58.0	46.0	53.0
10%	88.5	91.0	87.0	75.0	80.0
50%	106.0	97.0	109.0	100.0	105.5
90%	156.0	107.0	161.0	140.0	151.0
Boiling ends	202.0	119.0	208.0	173.5	210.0

As Table 6 shows, the extent of dehydrogenation on a rhenium–palladium–alumina catalyst activated with hydrogen sulphide is 87% for cyclohexane and 90% for methylcyclohexane, and 61.2% of benzene can be obtained from methylcyclopentane. Catalysts consisting of rhenium (or palladium) alone on alumina gave much lower conversions of the hydrocarbons than the mixed catalyst. Reforming of Baku light petroleum and other fractions[75,102] on rhenium–palladium–alumina catalysts treated with hydrogen sulphide raised the aromatics content 7–10-fold, and lowered the concentration of sulphur compounds by a factor of 1.4. The addition of 1% of rhenium to a palladium–alumina catalyst treated with hydrogen sulphide increases the stability of the catalyst under reforming conditions by almost a factor of 4. As Table 6 shows, mixed rhenium–palladium–alumina are also active towards isomerisation reactions. Thus, the yield of hexane isomers on a rhenium–palladium–alumina catalyst is 32%, and 52% on a rhenium–palladium–alumina catalyst treated with hydrogen sulphide. Whereas a 1% rhenium–alumina gives only 7% isomerisation of n-hexane, the sulphided catalyst gives 14% isomerisation[101]. There was no indication of a decrease in the isomerisation activity of the mixed catalyst after prolonged operation (90 h). The activity of a catalyst containing 1% of palladium but no rhenium had fallen by a factor of 2 after 50 h. Hence, the addition of 1% of rhenium to a palladium–alumina catalyst increases the stability of the catalyst very significantly. All these findings point to the high efficiency of H_2S-treated rhenium–palladium–alumina catalysts for dehydrogenation, dehydroisomerisation, and isomerisation reactions.

This catalyst was tested under static and fluidised bed conditions for reforming the 72–102° fraction of Karadag light petroleum[104]. The results, set out in Table 8, show that the concentration of aromatic hydrocarbons in the reforming product is 36–42% after 25 h operation under static or fluidised bed conditions. The concentration of benzene increases 4-fold, that of toluene 5-fold. The concentration of C_5 and C_6 alkanes remains almost constant. In the initial light petroleum fraction, the hexane isomers account for ~50% of the total content of hexanes. Thus, the aromatic hydrocarbons are formed mainly by dehydrogenation of six-membered cyclanes, with a much smaller contribution from the dehydroisomerisation of alkylcyclopentanes. In subsequent studies of the stability of the catalyst it was shown that in a static layer the activity gradually decreases, and after 40 h the concentration of aromatic hydrocarbons in the reforming product has fallen to 20%, whereas under fluidised bed conditions the concentration of aromatics has barely decreased at all (36%) after 100 h operation. It follows that the stability of the catalyst is approximately 4 times higher for the fluidised bed than for the static catalyst. A likely explanation is that the macroscopic surface area of the catalyst is much higher in the fluidised bed than in the static layer, and also that isothermal conditions are more rigorously observed in the fluidised bed. After 100 h the catalyst was regenerated by air under atmospheric pressure at 400° (fluidised bed), and treated with hydrogen. The experiments were made under 10 atm pressure, at a flow rate of 1.5–2 changes per hour, and 10 : 1 ratio of H_2 to hydrocarbons. Under these conditions, the concentration of aromatics in the reforming product was increased 5-fold (as previously). Thus, we may conclude that the rhenium–palladium–alumina catalyst treated with hydrogen sulphide regains its full activity on being regenerated.

Table 8. Properties of initial 71–102° Karadag light petroleum and of reforming products under static and fluidised bed catalytic conditions (480°, flow rate 0.8–3.5 h^{-1}, 10 atm pressure, H_2 : hydrocarbon ratio 5–20).

Composition of petroleum and reforming products, wt.%	Initial 71–102° fraction	Static bed	Fluidised bed	
		Reforming products after operating catalyst for		
		25 h		100 h
Isopentane	1.4	1.2	1.1	0.9
n-Pentane	2.7	2.1	2.5	1.9
2,2-Dimethylbutane	0.3	0.4	0.7	0.5
2-Methylpentane + 2,3-dimethylbutane	5.9	6.3	6.2	5.8
3-Methylpentane	4.8	3.9	4.6	4.4
n-Hexane	12.4	10.9	11.6	10.3
n- and Isoheptane + dimethylcyclopentanes + methylcyclopentane	48.9	36.7	30.7	37.4
Methylcyclohexane	15.4	1.1	0.8	2.8
Benzene	3.7	15.1	18.7	12.9
Toluene	4.5	21.3	23.2	23.0

This work on the reforming of hydrocarbon mixtures on catalysts containing rhenium justifies the conclusion that this element offers interesting possibilities as a component of dehydrogenation, isomerisation, and dehydroisomerisation catalysts, offering enhanced activity and stability.

Müller and Schnabel[105] studied rhenium–platinum catalysts on carbon in the dehydrogenation of cyclohexane and the "C_5-dehydrocyclisation" of iso-octane at 250–400° under atmospheric pressure. Koppers coke [a brown coat coke (Ed. of Translation)] was found to be a better carrier than birch charcoal. The activity of the carbon-supported platinum–rhenium catalyst showed a significant improvement only when 50% of platinum and 50% of rhenium was used, and the platinum was deposited first. Otherwise, the activity of the Pt–Re catalysts, though much

higher than that of rhenium catalysts, was somewhat lower than the activity of platinum catalysts. A maximum activity is found at Pt or Re concentrations between 0 and 1 wt.%, followed by a sharp fall in catalytic activity. An increase in activity occurs at 5% Re content (or 2.5% Re and 2.5% Pt in mixed catalysts). The activity of the catalysts towards the dehydrocyclisation of iso-octane is very sensitive to the preparative conditions. Thus, catalysts prepared by impregnating the carbon with a platinum solution, with subsequent hydrogen reduction, are less active than catalysts in which the platinum was reduced by the Zelinskii formalin–alkali method. The advantage of using Koppers coke lies in the constancy of its composition.

However, there is no prospect as yet of using these catalysts in industrial production because no suitable method of regeneration has yet been found. Hence, only oxide carriers such as alumina, silica, alumina–silica, zeolite, etc., are likely to be of importance in petroleum refining applications of rhenium catalysts.

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We have shown that specific areas of application of rhenium in the field of catalysis can already be identified, despite the fact that the chemistry of the element began to be studied only recently (since the 1930's), and systematic studies of its catalytic properties are of even more recent date.

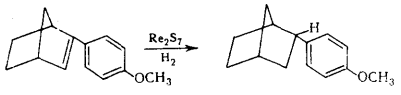
Rhenium catalysts can be of importance in the preparation of a number of rare organic compounds. For example, rhenium black[50] and $ReO.2H_2O$[55] are universal catalysts for the preparation of alcohols from ethanol to undecanol by reduction of the corresponding acids or ketones; the tetrahydropyran complex of Re_2O_7[52] and skeletal rhenium[56] are selective hydrogenation catalysts for the aromatic bond. The sulphides of rhenium have been found to have specific activity towards the dehydrogenation of alcohols to aldehydes and ketones[58,59], the reduction of the C=C double bond, the reduction of organosulphur compounds without cleavage of the C–S bond[59], of the azomethine group (C=N) without hydrogenation of the benzene or the thiophen ring[65,66], of carbonyl groups in aldehydes and ketones of the thiophen series[63,64], and the reductive alkylation of aromatic amines by ketones[67,69] without breaking the C–N bond or hydrogenating the ketone and the aromatic ring.

Lastly, addition of rhenium to hydrogenation catalysts[92,94-100] and reforming catalysts[101-104] produces a substantial improvement in the activity and stability of these catalysts. This observation may be important, and may lead to the practical use of rhenium catalysts in the chemical industry.

The recent paper by Davenport and coworkers[106], and our own very recent results, have had to be omitted from the present review.

Rhenium–alumina catalysts treated with hydrogen sulphide[107] are appreciably active in the dehydrocyclisation of diethyl sulphide to thiophen.

Rhenium heptasulphide reduces *p*-norbornenylanisole quantitatively to *endo*-norbornylanisole:



and also reduces the pyridine ring in substituted aryl-γ-pyridylmethanes and γ-arylpyridines.

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Zelinskii Institute of Organic Chemistry
USSR Academy of Sciences, Moscow

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Application of Mass-spectrometry to the Study of the Decomposition Kinetics and Mechanisms of Solids

O.P.Korobeinichev

The application of mass-spectrometry to the study of the decomposition kinetics and mechanisms of solids is discussed. Different designs of equipment and experimental procedures for studying the kinetics and the mechanism of the primary and the secondary processes in the decomposition of solids are described, and their relative advantages are analysed. Conditions likely to clarify specific aspects of universal importance to the decomposition of solids are formulated, and the advantages of dynamic mass-spectrometry in this type of study are stressed. The most important results of mass-spectrometric experiments on the kinetics and mechanism of the decomposition of solids are reviewed, including the thermal decomposition of inorganic solids, high-temperature reactions involved in the decomposition of solid propellants, the thermal and mechanical degradation of polymers, and other illustrations of the possibilities of the method.
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I. INTRODUCTION

Mass-spectrometry offers valuable information on the composition of materials and on the structure and concentration of molecules, and has an important part to play in the study of complex reaction mechanisms, since it helps to identify unstable intermediates such as atoms and radicals. The application of mass spectrometry to the study of radicals and their reactions in the gas phase and to the study of gas-phase kinetics has been discussed in a number of review articles[1-3]. More recently, mass spectrometry has been extensively used to study the kinetics and mechanisms of the thermal decomposition and evaporation of solids, including ionic and molecular crystals, metals and oxides, and also the pyrolysis of polymers, coal, and explosives. Recent work on the kinetics and mechanism of decomposition of solid propellants at temperatures close the surface temperatures encountered in combustion has made an important contribution to our understanding of the combustion of these solids. Valuable work is also proceeding on the ignition and combustion of solid propellants.

II. GENERAL FEATURES OF THE MASS-SPECTROMETRIC STUDY OF THE KINETICS AND MECHANISM OF THERMAL DECOMPOSITION OF SOLIDS

Studies of the initial stages of the formation and growth of nuclei, in which the amount of material undergoing chemical change is of the order of 0.1–0.001%, are of

fundamental importance to an understanding of the kinetics and mechanism of thermal decomposition of solids. The scope of this work has been considerably extended by the use of mass spectrometers for measuring partial pressures: modern mass spectrometers have extremely high sensitivities (up to 10^{-11} mmHg for Ar). Processes in the condensed phase can be monitored by using a mass spectrometer to determine the composition of the gas phase. Because of the very high sensitivity of the mass spectrometer, decomposition can be studied in single crystals, thus avoiding the complications associated with intercrystalline boundaries and gas diffusion.

The decomposition of many solids (formates, perchlorates, nitrates) is known to occur in different stages, some of which involve only the solid surface, giving rise to primary decomposition products, whilst the subsequent (or secondary) processes involve the gas phase or the solid/gas interface. Hence it is most important to distinguish primary from secondary processes, so as to study them separately and to identify their individual role in the overall process. In order to study only the primary decomposition stages of solids, and to exclude secondary reactions in the gas phase, the pressure in the reaction vessel must be low enough (10^{-4}–10^{-5} mmHg) to ensure that the molecular mean free path is large compared with the dimensions of the vessel. This condition is satisfied when the ion source of a mass spectrometer is used as the reaction vessel. In order to detect unstable, short-lived species such as atoms, radicals, and also molecules of compounds which are involatile at room temperature, and corrosive gases, the sample must be located very close to the ionisation volume (within a few millimeters). This requirement has been observed in most of the published work on the decomposition mechanism of solids (polymers, coal, ionic crystals, solid propellants, oxides).

The method of heating the solid sample deserves special mention: the powerful sources used for flash heating include xenon lamps[4,5], optical arc furnaces[4,6-8], lasers[9], and electrically heated metal strips[10-12] and gauzes[13-14].

Heating by radiation has the advantage that contact between heater and sample is unnecessary, uniform temperature can be obtained throughout the sample (for transparent samples), and fast heating rates (up to 10^6 deg s^{-1}) and high temperatures (several thousands of degrees with laser beams) can be achieved. However, sample temperatures are difficult to measure with these methods of heating. We have used[10-12] a very small sample of the solid ($\sim 10^{-6}$ g) resting on a titanium strip which was heated electrically, other workers[13,14] have used a platinum strip. Fast heating (in 10^{-3} s) was obtained by discharging a capacitor through the strip whilst passing also a continuous electric current to compensate for thermal losses. Temperature constancy (to within 1–2°) could be achieved by suitable choice of the capacitor voltage and of the constant current: this is particularly important in studies of the decomposition kinetics of solids under isothermal conditions. By using small samples (crystallites, or layers a few microns thick in good thermal contact with the heater strip) the heating time can be kept small (of the order of milliseconds) and the temperature gradients can be reduced to a fraction of a degree when heat is absorbed or evolved as a result of decomposition. The temperature of the heater strip (approximately 100 μm thick) was measured by a thin (5 μm diameter) thermocouple spot-welded or stuck to the strip with a heat-resistant cement. Fig. 1 shows the design of an apparatus used[11] to study the kinetics of the isothermal decomposition of solids by a time-of-flight mass spectrometer method.

The decomposition of coals has been studied[13] also under non-isothermal conditions. Coal particles of 60 μm diameter were placed on a grid with holes 50 μm in diameter, and heated at a constant rate of 10^3 deg s^{-1}. In contrast to the previous work[11], the temperature of the sample was varied linearly with time. Assuming first-order kinetics, all the kinetic parameters (activation energy and pre-exponential factor) could be derived from the results of a single experiment. However, because of the need to assume the kinetic order of the reaction, the method is less accurate than the isothermal method, which directly gives the reaction rate as a function of time. This is particularly important in studies of the decomposition of solids, when the reaction can show diffusional limitation or autocatalytic phenomena, and the problem of identifying the kinetic order becomes complicated or even meaningless.

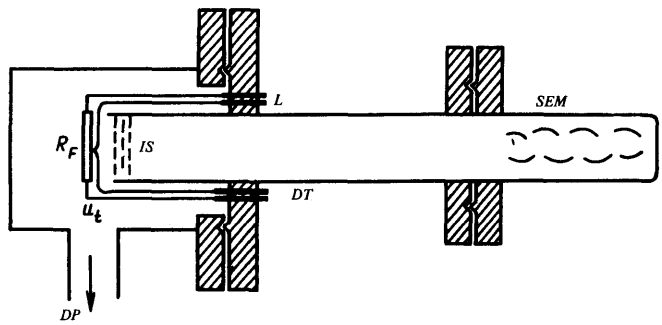

Figure 1. Location of the heater in the ion source of a time-of-flight mass spectrometer[11]: R_F, heater; u_t, thermocouple; *IS*, ion source; *DT*, drift tube; *SEM*, secondary electron multiplier; *L*, electrical leads; *DP*, diffusion pump.

The time constant of the mass spectrometer presents some problems in measurements of the kinetics of fast thermal decomposition reactions in solids. Thus, the most commonly used mass spectrometers, which rely on fixed magnets, can only be used for reactions extending over periods of hours, and their use at elevated temperatures is therefore severely limited. Therefore, dynamic mass spectrometers are far more useful in this type of work: they include time-of-flight mass spectrometers (which have no magnet, and a time constant of 10^{-5}–10^{-4} s), mass spectrometers with a permanent magnet and a variable accelerating potential ($\sim 10^{-2}$ s), quadrupole mass spectrometers, omegatrons, etc.

The design and the areas of application of time-of-flight mass spectrometers have already been discussed[15].

In kinetic studies of the decomposition of solids in the ion source of a mass spectrometer, the most important problem is to establish the relationship between the measured peak intensities and the rates of formation of the gases which contribute to these peaks (i.e. the reaction rates). When the reaction rate is comparable in magnitude to the pumping speed, the rate w_i of formation of the component i is related to the peak intensity I_i; this is proportional to the partial pressure of that component in

the ionisation volume if no other component contributes to the peak, according to the expression[16]:

$$w_i = A\left(\frac{dI_i}{dt} + KI_i\right)$$

where K is the pumping rate constant and A is a proportionality constant related to the sensitivity of the apparatus.

In the limit of a reaction rate much higher than the pumping speed this equation takes the form:

$$w_i = A\frac{dI_i}{dt}.$$

In the opposite limit, when the pumping speed is much higher than the reaction rate, the intensity of the appropriate peak is directly proportional to the latter:

$$w_i = AKI_i = BI_i.$$

In some recent studies[17,18] of the kinetics of polymer degradation using a time-of-flight mass spectrometer with stroboscopic presentation of the signal, which offers a substantially higher sensitivity[19], the constant B had the value $\sim 10^{11}$ molecules s^{-1}.

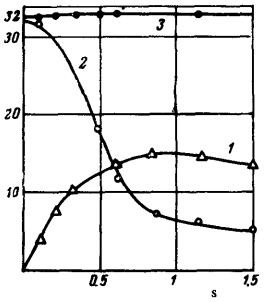

Figure 2. Time dependence at a constant temperature of 310° (see curve *3*) of the intensity of the mass 16 peak (curve *1*) and of the reaction rate (curve *2*), in relative units, during thermal decomposition of ammonium perchlorate in the ion source of a time-of-flight mass spectrometer[11].

Fig. 2, which was obtained in the writer's laboratory[11], shows the time dependence of temperature, intensity of the mass 16 peak, and reaction rate, all in relative units, measured in a study of the thermal decomposition of ammonium perchlorate in the ion source of a time-of-flight mass spectrometer under conditions of comparable pumping speed and reaction rate.

When the decomposition kinetics and mechanism of solids are studied at relatively high pressures (up to 1 atm), secondary reactions in the gas phase cannot be excluded. These add to the difficulty of quantitative mass spectroscopic analysis of gas mixtures (since the measured peak intensities are linearly related to partial pressures in the reactor irrespective of the composition of the gas only if the gas is mixed with a large proportion of an inert diluent) and to the other difficulties of studying gas kinetics a high pressures[1-3]. If the reaction is observed under static conditions, the diffusion time of the decomposition products to the sampling point (or orifice) must be much less than the reaction time. If the reverse is true, the measured rate will be the rate of diffusion of the products from the solid to the orifice rather than the reaction rate. The diffusion time can be significantly decreased by carrying out the reaction under flow conditions using an inert gas stream to carry the reaction products from the sample to the orifice.

Tauerman and coworkers[6-8] studied the volatile products evolved immediately before ignition of two-component solid propellants by a beam of radiation from an optical arc furnace. In this way, the distance between the fuel charge and the conical diaphragm was reduced to 5 mm, and the distance between the orifice and the ionisation volume was 19 mm. The vessel containing the charge was swept with helium at 10–200 mmHg pressure containing 1% of argon as an internal sensitivity standard. This precaution is essential, as the sensitivity decreases when the reaction rate is increased. The apparatus is shown in Fig. 3. The surface temperature of the charge was measured by a thin (50 μm) Chromel–Alumel thermocouple.

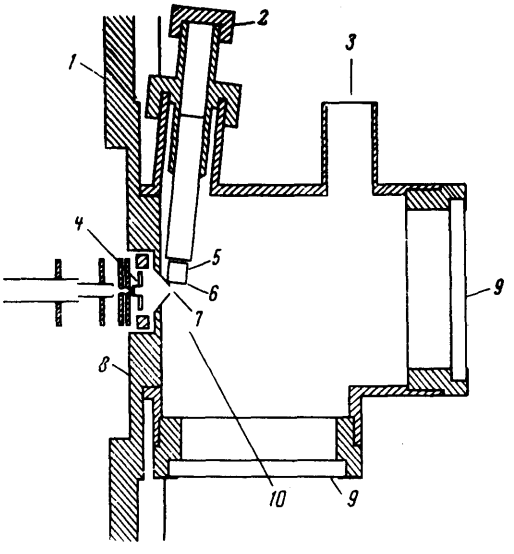

Figure 3. Combustion chamber combined with the ion source of a mass spectrometer[8]: *1*) upper flange of ion source; *2*) sample holder; *3*) to pump; *4*) electron beam; *5*) sample of propellant; *6*) thermocouple; *7*) orifice; *8*) ion source; *9*) quartz viewing port; *10*) radiation from optical arc furnace.

We shall now discuss the most important results obtained by the methods described, and consider concrete examples of the usefulness of the methods.

III. RESULTS OF MASS-SPECTROMETRIC STUDIES OF THE DECOMPOSITION KINETICS AND MECHANISMS OF SOLIDS

1. Decomposition of Inorganic Compounds

Many papers have been written on the thermal decomposition of ammonium perchlorate[10-12,20-24]. Heath and Majer[20], who were among the first to examine this system,

tried to identify the primary decomposition products of ammonium perchlorate in the ion source of a mass spectrometer at 100°. Unfortunately, they used large samples and were therefore unable to exclude secondary reactions in the pores of their sample, where the pressure was probably several order of magnitude higher than in the ion source. As a result, they detected several secondary products (H_2O, NO, NO_2, O_2, Cl_2) as well as the primary product (NH_3). Because of the large distance between the ion source and the sample, and of the modest pumping speed of their apparatus, the authors[20] failed to detect any perchloric acid in the mass spectrum. In order to analyse corrosive gases such as perchloric acid, chlorine, and hydrogen chloride, the time between their formation and detection must be much shorter than their lifetime. (These species disappear as a result of wall reactions.) This condition was evidently not fulfilled in Heath and Majer's work[20]. Since their mass spectrometer was of the static type, with a large time constant, the reproducibility of their results was also poor: the rate of change of the peak intensities was of the same order as the rate of scanning of the mass scale.

More reliable results were obtained in a later study[21] of the main products of the thermal decomposition of ammonium perchlorate at relatively low temperatures (230°). A time-of-flight mass spectrometer was used at pressure of the order of 10^{-3} mmHg. According to the authors[21], the ammonia and perchloric acid formed as primary products did not enter into secondary gas-phase reactions in the hot region of the reaction vessel, and they recombined in the cold regions with formation of NH_4ClO_4. This study included the decomposition of $^{15}NH_4ClO_4$ in order to distinguish the nitrous oxide peak from the background carbon dioxide. The main reaction products at 230° were found to be: water, nitrous oxide, chlorine, and oxygen, together with significant amounts of hydrogen chloride and nitrogen. Hence the equation suggested by Bircumshaw[25], giving H_2O, N_2O, Cl_2, and O_2 as the products, is not completely accurate. A later paper by the same authors[22], dealing with the decomposition kinetics of $^{14}NH_4ClO_4$, $^{15}NH_4ClO_4$, $NH_xD_{4-x}ClO_4$ at 160–230° and 10^{-4}–10^{-7} mmHg, gives the activation energy for the decomposition (28 kcal mole^{-1}) and the ratio of products ($O_2 : N_2O : Cl_2 = 3 : 3 : 2$).

The primary decomposition step of ammonium perchlorate and the decomposition kinetics in a vacuum have been studied in the writer's laboratory[10-12], using time-of-flight mass spectrometry and fast heating techniques. The primary decomposition products were found to be ammonia and perchloric acid. By using small samples (10^{-6}–10^{-5} g), the complicating effects of secondary reactions in the pores between crystallites of the sample were avoided, and the primary decomposition products were identified over the range 280–500°. This work showed that neither decomposition by electron transfer nor breaking of the Cl–O bond play a significant role, and that the main reaction is dissociation of ammonium perchlorate into ammonia and perchloric acid by the scheme

$$NH_4ClO_4(s) \rightarrow NH_3(g) + HClO_4(g), \quad (1)$$

followed by oxidation of the ammonia by the decomposition products of perchloric acid. The mass spectrum of the flash pyrolysis products of ammonium perchlorate is discussed by Boldyrev and coworkers[12]. The spectrum was recorded 1 ms after the onset of decomposition. The perchloric acid spectrum is practically indistinguishable from that obtained by Fisher[26] on an apparatus specially designed for the study of atoms and free radicals. Other papers also discuss the dissociation of ammonium perchlorate into ammonia and perchloric acid[11,27]. The experimental method of studying the kinetics of this reaction has already been described in the previous Section. Ammonium perchlorate crystallites of 10 μm diameter were deposited on the heater strip by evaporation of a droplet of an aqueous or alcoholic solution of ammonium perchlorate. The following relationship was found between the maximum decomposition rate $\left(\frac{d\alpha}{dt}\right)_{max}$ and temperature over the range 280–320°:

$$\left(\frac{d\alpha}{dt}\right)_{max} = 10^{9.09}\exp(-24\,000/RT)\ s^{-1}.$$

Combining this result with data[28] on the equilibrium pressure of ammonia and perchloric acid vapour we obtain a sublimation coefficient $\beta = 8 \times 10^{-2}$ for ammonium perchlorate, which is only a factor of 2 higher than the value reported[29] for the range 230–270° by a different method. The activation energy is lower than a previously published value[29] by 6 kcal mole^{-1}, but higher than another reported value[30] by 2.5 kcal mole^{-1}.

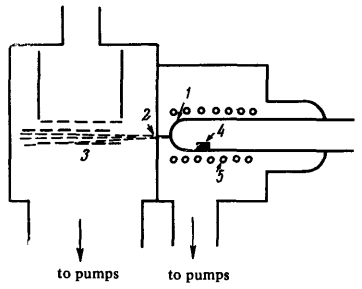

Figure 4. Mass spectrometric assembly for studying the decomposition of solids in the vicinity of the ion source at relatively high pressures[24]: *1*) orifice; *2*) diaphragm; *3*) ion source of time-of-flight mass spectrometer; *4*) sample; *5*) furnace winding.

The decomposition of ammonium perchlorate has been studied[24] at 400° and 20–100 mmHg pressure, i.e. under conditions which did not exclude secondary gas-phase reactions. The combined reaction vessel and effusion orifice used in this work was of molybdenum glass, previously heated to the required temperature. The distance between the orifice and the ionisation volume was a few millimeters, the pumping speed was ~ 100 litre s^{-1}. As a result, unstable particles and corrosive gases could be reliably monitored. The sample was inserted into the heated reaction vessel by magnetic "ram" (Fig. 4). It was located 10 mm from the orifice, and therefore the diffusion time of gas molecules from the sample to the orifice was as short as 0.05 s at 8 mmHg and 0.5 s at 80 mmHg. Because of the shortness of the diffusion path, the procedure allowed the primary decomposition products of ammonium perchlorate (ammonia and perchloric acid) to be detected as well as the secondary products (chlorine, oxygen, nitrous oxide, water, nitrogen, nitric oxide, hydrogen chloride). The measured concentrations of ammonia and perchloric acid were practically the same as the reported[28]

equilibrium pressures of ammonia and perchloric acid over solid ammonium perchlorate:

$$NH_4ClO_4(s) \rightleftharpoons NH_3(g) + HClO_4(g). \quad (2)$$

This confirms the decomposition scheme for ammonium perchlorate proposed by the writer[27] and the hypothesis that the equilibrium corresponding to reaction (2) is maintained during the decomposition. Changes in gas phase composition during the reaction were also observed in the absence and in the presence of iron oxide, and correlated with the catalytic effect of impurities on the dissociation of nitrous oxide.

The dissociation of perchlorates other than ammonium perchlorate has also been investigated. Thus, the kinetics of the thermal decomposition of nitronium perchlorate NO_2ClO_4 has been studied[31] at 100–160° at pressures high enough for the secondary reactions to be significant. The decomposition products are O_2, NO, and Cl_2, the activation energy 15 kcal mole^{-1}. The primary stages in the decomposition of guanidinium perchlorate have been investigated[32] in the ion source of a time-of-flight mass spectrometer. In addition to the reaction previously proposed[33],

$$CH_5N_3 \cdot HClO_4 \rightarrow CN \cdot NH_2 + HClO_4 + NH_3 \quad (3)$$

it was shown that guanidinium perchlorate dissociates by the reaction

$$CH_5N_3 \cdot HClO_4 \rightarrow CH_5N_3 + HClO_4. \quad (4)$$

One-third of the material dissociates by reaction (3), and two-thirds by reaction (4).

An omegatron has been used[34] to study the decomposition of ammonium polymolybdate and polytungstate; ammonia, and molybdenum and tungsten oxides, have been identified as the decomposition products. The accompanying hydrogen and nitrogen are assumed[34] to result from the catalytic decomposition of the ammonia pumped through a layer of molybdenum or tungsten oxide.

The products of the pyrolysis of nickel tetracarbonyl and iron pentacarbonyl have been investigated[35,36]. The mass spectrum of $Ni(CO)_4$ positive ions was established in the mass spectrometer by a method which allowed the molecular beam to be distinguished from the decomposition products formed in the ion source. The evidence for the existence of gas-phase intermediates such as $Ni(CO)_3$ could not be confirmed by sampling the gas from the low-pressure reactor. Appearance potentials and dissociation energies were obtained for the ions $Ni(CO)_x^{+q}$ ($q = 1.2$; $x = 1, 2, 3, 4$).

Bowden and coworkers[37] made a mass-spectrometric study of the kinetics of the thermal dissociation of sodium and thallium azide single crystals. They showed that in the initial stages of dissociation of small NaN_3 single crystals in a vacuum of 10^{-9} mmHg (i.e. close to the ion source of the mass spectrometer) various gases are evolved, such as Ne, Ar, He, and H_2, which are strongly held on the crystal surface by adsorption forces. Subsequently, when the nitrogen lines begin to appear in the mass spectrum, the residual OH^+ and CO_2^+ peaks disappear, obviously as a result of reactions between the background gases and the Na atoms formed by decomposition of the azide. The long induction periods frequently observed in the decomposition of solids can perhaps be ascribed to the disappearance of metal nuclei by reaction with the residual gases.

Many papers, only some of which are mentioned here[38–40], deal with the evaporation mechanism of solids and with the composition of their vapour. Thus, Shchukarev and coworkers[38] have studied the composition of the vapour over the oxides of gallium, thallium, and indium, Mostovskii and Sakseev[39] have examined the vapour over Sb_2S_3 and GeSe. Studies of the evaporation of GeSe have confirmed the view that this compound undergoes little dissociation in the vapour state. The vapours of many solids contain monomers, dimers, and trimers. Due to superposition of the lines, their ratio is often difficult to determine mass-spectrometrically.

Using a time-of-flight mass spectrometer[41,42], the following species have been detected by rapidly heating to 1400–3000° a tungsten wire which had been kept at room temperature in an oxygen atmosphere: O, WO, WO_2, WO_3, W_2O_6, and W_3O_9. These results indicate that only a few per cent of the surface tungsten atoms are oxidised at room temperature. The evaporation products include monomers, dimers, and trimers of WO_3. The activation energy for the evaporation of these oxides is ~ 100 kcal mole^{-1}.

2. Thermal and Mechanical Degradation of Polymers

The kinetics and mechanism of polymer degradation have attracted a great deal of study. Thermal degradation of polymers is known to give rise to a mixture of products of different volatilities[43]. Bradt and coworkers[44,45] published the first papers on the nature of the fractions which are involatile at room temperature but volatile at the temperature of the thermal degradation experiment. In this work, the polymers were decomposed in the immediate proximity of the ion source of a mass spectrometer. The thermal decomposition of polystyrene was shown[44] to produce dimeric and trimeric molecules in addition to the monomer. Analogous results were obtained in a study[46] of the decomposition of polyethylene at 200–330°. The mass spectrum consists of lines which can be assigned to C_nH_{2n+1} ions. The C_4H_9 peak is the strongest in the mass spectrum of the decomposition products of polyethylene at 200°. As the temperature is raised from 200 to 330°, the intensity maximum tends to flatten out and to shift from $n = 4$ to $n = 8$. The degradation is shown to proceed in two stages. In the first stage, mainly at the lower temperatures (~ 200°), the rate is limited by diffusion of light molecules through the polymer. In the second stage, at higher temperatures, the thermal degradation is rate-limiting. The decomposition products of poly(tetrafluoroethylene) and poly(fluoroethylpropylene) have been studied[47] at 350–875° with a time-of-flight mass spectrometer; the flash-pyrolysis products of various polymers have also been studied[16] using a fast pulse of energy from a high-power xenon flash tube. The experimental problems encountered in the study of polymer degradation by mass spectrometry have been discussed in a number of papers[48–50].

The time-of-flight mass spectrometer has been used[17,18,50–53] to study the kinetics and mechanism of the mechanical and thermal degradation of polymers. The polymer samples were fractured and heated close to the ion source of a mass spectrometer, as shown in Fig. 5.

The primary products of the thermal and the mechanical degradation of poly(methyl methacrylate) and polystyrene were shown[51] to have identical mass spectra. Hence it was concluded that the gas evolution accompanying mechanical degradation of these polymers has a thermal origin: the polymer suffers local heating during fracture, and gases are evolved as a result of the rise in temperature. Regel' and Muinov[18] showed that gases are evolved as soon as the load is applied, not only after fracture of the polymer sample. This suggests that decomposition of the polymer sets in as soon as the load is applied. Since the

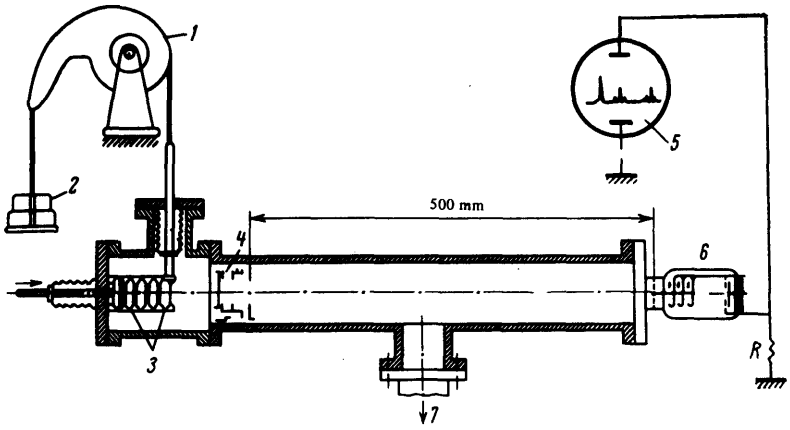

Figure 5. Apparatus for studying the kinetics and mechanism of mechanical degradation of polymers by a time-of-flight mass spectrometric method[52]: *1*) cam; *2*) load; *3*) sample magazine; *4*) source; *5*) mass spectrum; *6*) electron multiplier; *7*) to vacuum pump.

curves of elongation and gas evolution against time are identical, the degradation and deformation processes must be intimately related. The rate of gas evolution is an exponential function of the applied stress. Amelin and coworkers[53] have reported studies of the thermal and mechanical degradation of poly(methyl methacrylate), polystyrene, poly(vinyl chloride), polypropylene, and polyacrylonitrile. They show that the volatile products of thermal and mechanical degradation are identical if the decomposition of the polymer begins in the main chain. When thermal degradation of the polymer involves the removal of side chains, the volatile products are different from those of mechanical degradation. These findings confirm and extend the results of the kinetic theory of degradation, according to which the mechanical fracture processes are related to the thermal degradation of polymers. In a kinetic study[17] of the thermal degradation of poly(methyl methacrylate) and of the methyl methacrylate monomer, initially the activation energy is found to be 30 kcal mole^{-1}, but at a more advanced stage of degradation it becomes ~ 50 kcal mole^{-1}.

3. High-temperature Decomposition of Solid Propellants

Valuable information on the mechanism and the kinetics of the high-temperature decomposition of solid propellants, which play an important part in combustion, can be obtained by fast heating of solid samples to elevated temperatures, and by identifying the decomposition products (including unstable species) in a dynamic mass spectrometer such as a time-of-flight or other instrument with a short time constant. The kinetic parameters of the decomposition reaction can be obtained from a mass spectrometric study of the rate of formation of these products[23]. As a result of the recent developments in the relevant experimental techniques, this type of work has grown considerably in the last few years.

We shall take as our first example a study[4] of the pulsed pyrolysis of nitrocellulose. The source of heat was radiation from an optical arc furnace. Both the characteristics of the source of heat[4,54,55] and the unstable intermediates found in the pulsed pyrolysis of solid organic compounds[4,56,57] have already been described. However, unequivocal identification of these products is far from easy. One of the most important results of this work is the realisation that the composition of the pyrolysis products of cellulose is a function of the rate of heating: this is evident from the data summarised in the Table. For low heating rates up to 300°, using conventional resistance heating, the main decomposition products are water, solid carbonaceous deposits, and volatile organic compounds.

Pyrolysis products of cellulose[4].

Heat source	Electric furnace	Carbon arc	Carbon arc	Xenon flash tube
Thermal flux, cal cm^{-2} s^{-1}		1.5	11	3000 at peak of output
Temperature, °C	up to 350	300	600	600
Heating time	2.7 h	10 s	4 s	$5\cdot10^{-4}$ s
Atmosphere	vacuum	helium	helium	helium
	Products (in wt.%)			
H_2O	19	32	16	28
CO	3	3	13	37
CO_2	?	9	11	4
Volatile organic compounds	51	3	6	30
Tar	2	19	51	none
Solid carbonaceous residue	25	33	3	1
CO/CO_2 ratio	—	0.33	1.2	9.2

With the higher heating rates obtainable from an optical arc furnace (heating time 4–10 s), a large amount of tar is formed and the yield of volatile organic compounds decreases. Under flash pyrolysis with a xenon lamp (heating time ~ 0.5 ms) the main products are volatile

organic compounds (mainly aldehydes and ketones), water, and carbon monoxide. As the heating rate is increased, the CO/CO_2 ratio increases and the molecular weight of the products decreases. Fast heating appears to subdivide the polymer chains into smaller segments. Evidently, pyrolysis in the condensed phase is accompanied by a whole spectrum of chemical reactions in series and in parallel whose probability depends on the heating rate. Useful products can be obtained by controlling the heating rate. Similar effects have been observed during the carbonisation of coal.

The use of a pulsed laser beam for heating coal particles is a new and interesting technique in this area of research[9]. Very small particles of coal (less than 10 μm in diameter, $\sim 10^{-6}$ g) were placed in a quartz tube within the ion source of a time-of-flight mass spectrometer about 10 mm from the ionisation volume, and heated by a pulse of radiation from a focussed laser beam. The energy of the pulse was 0.7 J, corresponding to an energy flux of $\sim$ 100 kW cm^{-2} for a spot diameter of 7 mm. The mass spectrum was recorded 0.2 ms after application of the pulse of radiation. In addition to the stable decomposition products, including polyacetylenes, free radicals (H, C, CH_3) and alkali metal ions (Na^+, K^+) were observed. The mass spectra obtained at low energies of the ionising electrons provide further evidence of the formation of radicals and ions. The temperature of the spot could not be estimated, but it must have reached several thousand degrees, since a considerable amount of atomic carbon was found in the gas phase. The techniques used in this work are suitable for the detection of atoms and radicals in other high-temperature decomposition reactions.

Methods for studying the decomposition of coal under non-isothermal conditions have been developed[13]. The heating rate must be constant, or a known function of time. The method was tested on simple decomposition reactions of solid organic acids, giving rise to water, carbon monoxide, and carbon dioxide, and satisfactory agreement between theory and experiment was obtained. A resistance furnace was used for low heating rates (0.5–0.3 deg min^{-1}), and the decomposition products were led to the detector (a conventional mass spectrometer) by a stream of inert gas. A platinum gauze heater was used for higher heating rates (10^3–10^5 deg min^{-1}), and temperatures were measured by a platinum/platinum–rhodium thermocouple. The decomposition was studied close to the ion source of a time-of-flight mass spectrometer. The highest temperature was 1000°. Assuming first-order kinetics for the formation of ethane by the decomposition of coal, an activation energy of 42.1 kcal mole^{-1} and a pre-exponential factor of 10^{11} min^{-1} were obtained. It was shown that the evolution of methane and hydrogen from coal during pyrolysis is not a first-order reaction, but follows more complex kinetics. The theoretically predicted shift of the maximum reaction rate towards higher temperatures at higher heating rates was confirmed experimentally. Perhaps as a result of the arbitrary assumption of first-order kinetics, the error in the determination of rate constants was as high as two orders of magnitude.

A more satisfactory method of studying the kinetics of fast reactions relies on isothermal conditions, combined with the use of a time-of-flight mass spectrometers[10,11]. The method was applied[58] to kinetic studies of the mechanism of high-temperature decomposition of nitrocellulose. The rates of formation of various decomposition products (NO_2, CH_2O, H_2O, CO, and CO_2) have been studied[58] as a function of reaction time at temperatures (220–280°) close to the surface temperature of pyroxylin guncotton. The reaction was shown to be autocatalytic. The maximum decomposition rate, measured from the rate of formation of the mass 30 peak, is described by the equation

$$W_{max} = 10^{14.4} \exp(-35000/RT)\ s^{-1}.$$

Extrapolation to 220° of the rate of decomposition of nitrocellulose measured[59] at 130–160° in a vacuum of $\sim 10^{-4}$ mmHg (i.e. close to the experimental conditions of the previous investigation[58]) gives a value about an order of magnitude lower than reported in that work[58]. This may be due to a difference in the thickness of the nitrocellulose samples used in the two investigations ($\sim$ 3 μm in Ref. 58, and very much thicker in Ref. 59). The activation energy given in Ref. 58 is lower than the value obtained by other methods[59–61]. The difference may be ascribed to the different methods used to measure the rate constant. In Ref. 58, NO_2, CH_2O, CO, CO_2, and H_2O are chosen as the primary decomposition products although their relative amounts vary during the course of the reaction. The mass spectra of the decomposition products suggest that other nitrogenous species are formed in addition to NO_2 (possibly NO_3).

A series of papers by Dauerman and coworkers[6–8,62] discusses the primary act in the decomposition of nitrocellulose, nitroglycerine, and propellants based on these compounds, under low-pressure combustion and ignition conditions. Their experimental procedure, using a mass spectrometer with a variable accelerating potential has already been discussed (see Fig. 3). Since these experiments were made at relatively high pressures (10–100 mmHg), i.e. under conditions which permit secondary reactions in the gas phase, these workers' claims to have investigated the primary decomposition and combustion products are, to say the least, suspect. Thus, mass spectrometric data on the composition of the high-temperature pyrolysis products of nitrocellulose are quoted[7] in the presence of 10–100 mmHg pressure of helium. Radiant energy from an optical arc furnace is used, and the products are monitored immediately before ignition, at ignition, and during combustion. From an analysis of the intensity ratios of the mass 30 and 46 peaks, they conclude that nitric oxide is predominant among the primary decomposition products, with the reservation that the NO in their experiments could have been formed by decomposition of NO_2. Comparing these results with others[58], obtained under conditions which precluded secondary gas-phase reactions, we conclude that the nitrogen dioxide in Dauerman's experiments[7] must have been converted into NO before reaching the detector. These experiments give no information on the rate of formation of the various components as a function of the extent of conversion of the condensed phase, and in this respect also they differ from our own[58], since they were carried out under non-isothermal conditions of continuously rising temperature. However, in spite of these shortcomings, Dauerman's results[6–8] are very interesting because they reveal the correspondence between the surface temperature of the propellant and the rate of decomposition, thus increasing our knowledge of the processes involved in the ignition and combustion of solid propellants. They lead to the conclusion[6,8,62], very important from the standpoint of the theory of combustion of two-component solid propellants (consisting mainly of nitroglycerine and nitrocellulose), that the main product of the ignition and combustion of these propellants is the NO_3 radical and not NO_2, as previously suggested. This conclusion is based on the fact that the intensity ratio of the mass 46 and mass 30 peaks for the ignition and combustion products at 10 mmHg pressure was well above unity, and that no peaks above mass 46 were found in the

mass spectrum. Fig. 6 shows the time dependence[8] of the intensity of the main ion peaks, which are proportional to the rate of formation of the corresponding gaseous components during ignition of the propellant. The singularities on these curves (points where the differential shows a break) correspond to the moment of ignition and onset of combustion.

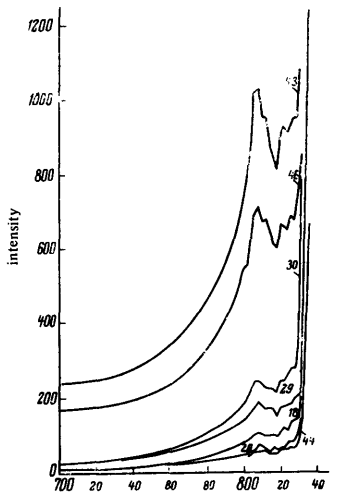

Figure 6. Intensity of various mass peaks as a function of time of irradiation during ignition of solid propellants by radiant energy[8]. The number of ciné-film frames, which is proportional to time, is plotted horizontally. The sample is an uncatalysed D-4 propellant.

Comparing Dauerman's mass spectrum[6,8] with published mass spectra of nitrate esters and other nitro compounds[63], including nitroglycerine, we conclude that it cannot be assigned to any known nitro ester. The mass spectrum was therefore assigned to the NO_3 radical, with the assumption that removal of this radical is the first step in the decomposition of two-component solid propellants (and also of nitroglycerine). However, this conclusion is also debatable, since the observed mass spectrum[6,8,62] could be due to a species (possibly even NO_3) resulting from secondary reactions in the gas phase, e.g. from the gas-phase decomposition of nitroglycerine, which is volatile under the experimental conditions used in that work[6,8,62]. The writer's mass-spectrometric study of the primary products of the decomposition of nitroglycerine compositions at 170–290° in a high vacuum, i.e. in the absence of gas-phase reactions, is also inconsistent with that conclusion[6,8,62]. The value of the mass spectroscopic method in studies of the decomposition of solid propellants is clearly shown in two papers by Dauerman and coworkers[8,64]. Lead stearate—an efficient catalyst for the combustion of two-component solid propellants—is shown[8] to catalyse other condensed-phase chemical reactions of these propellants. The role of the emulsifier in mixed solid propellants based on a butadiene–acrylic acid copolymer has been studied by a similar method[64].

Coats[65] also used the pulsed mass spectrometric method in his study of the thermal decomposition of mixed solid propellants based on ammonium perchlorate. In that work (quoted by Friedman[66]), a thin platinum wire coated with a film (5 μm thick) of the mixed solid propellant was heated to 500–600° in 50 ms by discharging a condenser, and the decomposition products were led to the ion source of a time-of-flight mass spectrometer. Peaks corresponding to hydrocarbon residues, NH_3, $HClO_4$, HCl, and ClO_2 were observed in the mass spectrum.

Recently published work[63,67–73] on the mass spectra of the molecules of individual explosives should prove very valuable in the interpretation of the mass spectra of the decomposition products of solid propellants.

Mass spectrometry has been widely used in recent years to study the kinetics and mechanism of the thermal decomposition of solids. Further developments are being constantly reported, and new fields of application in science and technology are being suggested. The method should prove valuable in areas such as cosmochemistry, the interaction of powerful light beams with matter, and also the study of the combustion mechanism of solid propellants and associated high-temperature, fast reactions. Many unsolved problems remain in all these fields.

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Institute of Chemical Kinetics and
Combustion, Siberian Section of the
USSR Academy of Sciences,
Novosibirsk

U. D. C. 547.62

Poly(arylenealkyls)

I.I.Yukel'son and V.S. Glukhovskoi

Information on the preparation of poly(arylenealkyls) by polycondensations and on their chemical reactions is surveyed. The chemical reactions of poly(arylenealkyls) can lead to the preparation of materials and products interesting in practical and theoretical respects. There are 75 references.

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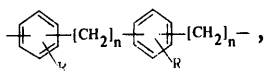
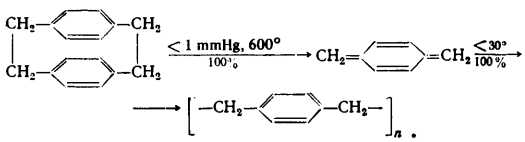
1. INTRODUCTION

It is now known that the methods, mechanism, and conditions of synthesis determine the significant features of the structure of a polymer chain, its structure and the properties of the polymer articles. This is well illustrated by the example of the poly(arylenealkyls)—polymers which contain benzene rings in a chain separated by methylene groups, of the general formula



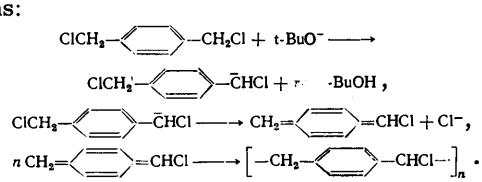
where $n \geqslant 1$ and R = H, CH_3, C_2H_5, C_3H_7, halogen, etc. Poly-(*p*-phenylene-ethylene) prepared by pyrolysis of *p*-xylene, was found to be less thermostable than the same polymer obtained by the reaction of phenyl-lithium with *p*-bisbromomethylbenzene[1]. A considerable number of methods for making such polymers is known and we will only point out some of them.

The preparation of poly-(*p*-xylylene) by the thermal decomposition of di-(*p*-xylylene) in vacuo at 600°C has been described[2]. First two molecules of the intermediate reactive *p*-xylylene are formed, which are spontaneously converted into linear poly-(*p*-xylylene) by the scheme:



Apart from di-(*p*-xylylene), dichloro-, dibromo-, dicyano-, dimethyl-, diethyl-, and tetrachloro-substituted di-(*p*-xylylene) can be used as the initial monomers. Linear, high-molecular-weight sparingly soluble polymers with good physico-mechanical and dielectric properties are formed[3]. Poly-(*p*-xylylene) can be obtained by heating $\alpha\alpha'$-dihalogeno-substituted *p*-xylene with nickel or cobalt powder in the presence of water[4].

A recent paper describes the synthesis of polymers of the poly-(*p*-xylylene) type by the polymerisation of halogenated *p*-xylenes in the presence of bases[5]. α-Chloro-*p*-xylene, by reacting with potassium t-butoxide (t-BuOK), gives poly-(α-chloro-*p*-xylylene) by the following series of reactions:



The polymers thus obtained exhibit considerable thermal stability and good physico-mechanical properties.

The preparation of poly-(*p*-xylylenes) by the electrolytic reduction of $\alpha\alpha'$-dihalogeno-*p*-xylenes has been proposed[6].

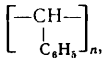
Several investigators[7] have prepared poly-*p*-xylylene with high thermal stability and chemical resistance by heating *m*-methylbenzyltrimethylammonium halides and metal hydroxides in alcohol medium then heating the product in hydrocarbons.

The simplest method for obtaining polymers containing a chain of benzene rings separated by methylene groups is the polycondensation of benzyl chloride and its derivatives, and also of dihalogenoalkanes with aromatic derivatives in the presence of Friedel–Crafts catalysts. However, the poly(arylenealkyls) thus obtained are strongly branched and have a comparatively low molecular weight and low physico-mechanical properties, unlike poly-(*p*-xylylenes).

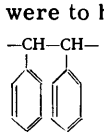
2. SYNTHESIS OF POLY(ARYLENEALKYLS) BY THE FRIEDEL–CRAFTS REACTION

The preparation of polymers with a chain of benzene rings separated by methylene bridges, has been known for a long time. Perkin[8] reported that benzyl chloride reacts with aluminium chloride to form resins and hydrogen chloride. The polycondensation of benzyl chloride has been studied most fully not only in the presence of Friedel–Crafts catalysts, but also of strong acids[9], and even in the presence of such an inert substance as glass[10].

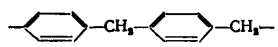
Many workers thought[10,11] that the polybenzyl formed should have a structure of the



type, but did not give any proof in support of this. Mass-spectroscopic analysis of the pyrolysis products of polybenzyl showed that they consist of toluene, benzene, and xylene[12]. If polybenzyl were to have the structure

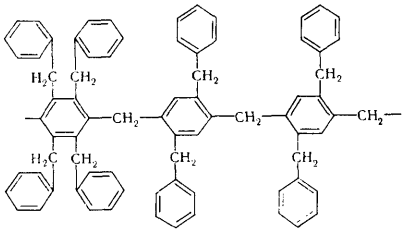


and not



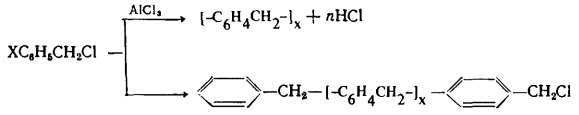
(both structures correspond to the same empirical formula $[-C_7H_6-]_n$) then one of the products of destruction should

be stable. The absence of stilbene shows that the linear structure is correct for polybenzene. The linearity of the polybenzyl structure is also shown by its high thermal stability. In this molecule where the phenyl groups do not enter into the composition of the main chain and there are substituents at each successive carbon atom, all the carbon–carbon bonds of the chain should be weakened by the presence of tertiary carbon atoms. The presence of benzene nuclei in the main chain of the polymer is responsible for its high stability because of the possibility of conjugation. The reason for the high thermal stability of polybenzyl could be a strongly branched structure, which was proposed because of the X-ray diffraction analysis and the infrared spectra:



In pyrolysis of polybenzyl the proportion of volatiles amounts to almost 100%, which shows the absence of a cross-linked polymer or at least of one strongly cross-linked.

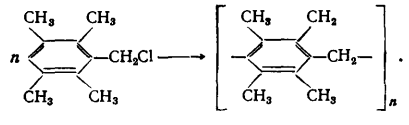
Korshak and coworkers [13] obtained polybenzyl by the polycondensation of benzyl chloride under the action of various Friedel–Crafts catalysts. It was found that in the presence of $AlCl_3$ a powdery product was formed, only partly soluble in benzene, with a softening point of 220–230°C and molecular weight 2000. In the presence of $ZnCl_2$ and $SnCl_4$ a powdery polymer soluble in benzene is formed. The polycondensation proceeds with the formation mainly of a linear polymer:



Owing to secondary alkylation of the same benzene ring the polymer can be branched and the formation of dihydroanthracene rings is possible.

By using the $AlCl_3$.nitrobenzene complex Moore [14] obtained polybenzyl and polyphenethyl with molecular weights not exceeding 1880 by the polycondensation of benzyl chloride and phenethyl chloride in nitrobenzene solution.

Haas [15] showed that the polymer obtained from chloromethyldurene is highly crystalline and has a completely linear structure, unlike the strongly branched and amorphous polybenzyl. The explanation for this difference in the properties of the polymers is that in the polymer based on chloromethyldurene all the positions of the benzene ring except *para*- are blocked:

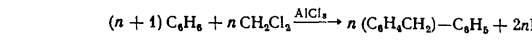


Overhults and Ketley [16] investigated the effect of substituents in the benzene ring of a chloromethyl-substituted monomer on the formation of a linear polymer. Copolymers of dichloromethyldurene and aromatic compounds were obtained in solution in the presence of $TiCl_4$ catalyst. It was found that if the number of methyl groups present in the second monomer is reduced from 4 (durene) to 2 (*p*-xylene) and to zero ($\alpha\alpha'$-dichloro-*p*-xylene) but the number of methyl groups in the first monomer remains at 4 then the polymers formed are crystalline, insoluble in organic solvents, and have low molecular weights (the degree of polymerisation does not exceed 8). However, when the aromatic ring does not have a substituent, for example, in the copolymerisation of $\alpha\alpha'$-dichloro-*p*-xylene with *p*-xylene, an amorphous product is formed, insoluble in organic solvents and not melting above 500°C. The properties of the polymer show that branching followed by cross-linking occur during the reaction. The polymers obtained from dichloromethyldurene and aromatic compounds in which methyl groups are in positions ensuring *ortho*- and *meta*-addition of the copolymer (for example, a copolymer of dichloromethyldurene) have a small amount of a crystalline product insoluble in benzene and a large amount of amorphous, soluble, low-melting product with degree of polymerisation 4–5. The formation of a low-molecular-weight polymer is evidently due to steric hindrance. If the number of blocking groups is reduced sufficiently to remove the steric hindrance the chain growth prevents cross-linkage. The maximal molecular weight of the soluble polymer is reached immediately before the start of cross-linking. On carrying out the reaction to partial cross-linking, the molecular weight of the soluble part falls from 3800 to 2000 and less. This shows that the longer chains of the polymer are cross-linked first. Attempts to inhibit cross-linking in polycondensation for the preparation of a higher-molecular-weight polymer did not lead to the desired result since chain growth ceases during this.

The polymer obtained from $\alpha\alpha'$-dichloro-*p*-xylene and *p*-xylene can, after separation and purification, be moulded at 120–140°C.

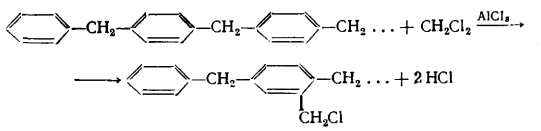
Crystalline polybenzyl, poly-(2,5-dimethylbenzyl), and poly-(α-methylbenzyl) were made by adding a solution of $AlCl_3$ in ethyl chloride to benzyl chloride or to 1-chloroethylbenzene respectively at ~ −130°C. [17] The X-ray powder diagrams of the polymers show their linear structure and high crystallinity. The linear structure is confirmed by an analysis of their infrared spectra (the absorption band of 1,4-disubstituted aromatic rings is at 805 cm^{-1}), and also of the NMR spectra, in which there are signals of aromatic protons with chemical shift 7.05 and methylene protons with 3.08, with relative intensity 2 : 1, which corresponds with the structure $H-[-C_6H_4CH_2-]_n$ for polybenzyl.

High-melting-point crystalline polybenzyls are obtained from benzyl chloride and its derivatives in the presence of $AlCl_3$ at −100°C. The best results in the low-temperature Friedel–Crafts reaction are also obtained with substituted benzyl chloride. Whereas polybenzyl has maximal m.p. 142°C, poly-(2,5-dimethylbenzyl) softens only at 190°C and melts above 300°C. [18] A polymer of the polybenzyl–poly(phenylenemethyl) (PPM) type can be obtained also by the polycondensation of benzene with methylene dichloride in the presence of $AlCl_3$: [19]

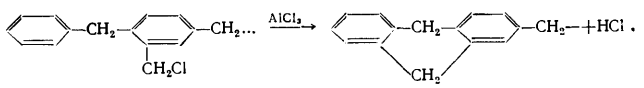


During the polycondensation cross-linked products are not formed at any ratio of the reactants. The reason for

the arrest of chain growth is the formation of dihydroanthracene terminal groups. It is thought that initially branched PPM molecules of the type:



are formed, although compounds with a terminal $-CH_2Cl$ group were not observed. The interaction of the chloromethyl group with a neighbouring aromatic nucleus leads to the formation of a dihydroanthracene ring:



The highest molecular weight of a polymer, 2970, was obtained at a methylene dichloride : benzene ratio of 3.12 : 1 and a catalyst concentration of 4.3 mole %. PPM is a viscous liquid and is soluble in halogenoalkanes and aromatic hydrocarbons.

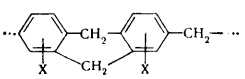
The possibility of the preparation of PPM [20] by the complete arylation of diphenylmethane under the action of $AlCl_3$ by the reaction:

has been shown[20]. The low-molecular-weight product of the complete arylation of diphenylmethane is benzene.

A polymer with the low molecular weight of 1350 is evidently obtained because of the formation of dihydroanthracene rings at the ends of the growing chains which leads to the arrest of chain growth.

The formation of a cross-linked product was observed only on raising the reaction temperature to 170 °C. Increasing the catalyst concentration also leads to an increase in the yield of PPM but an increase in the molecular weight is not observed.

Linear polymers with a molecular weight not exceeding 2500 were obtained by the polycondensation of fluorobenzene, chlorobenzene, and bromobenzene with methylene dichloride[21]. This shows that the activity of halogenobenzenes is less than that of benzene. It could be expected that the formation of dihydroanthracene rings at the ends of the growing polyhalogenophenylenemethyl chains leads to the breaking of the chain

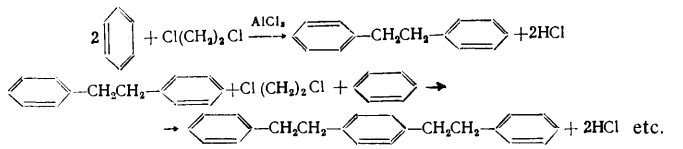


where X is a halogen atom.

A high-molecular-weight polymer is also not formed in the polycondensation of *p*-xylylene dichloride with various aromatic hydrocarbons in the presence of $SnCl_4$ in nitrobenzene at 60 °C. Only gelatinous polymers were obtained[22].

Polymers with benzene rings in a chain separated by $-CH_2-CH_2-$ groups are obtained by the polycondensation of 1,2-dichloroethane with benzene and its derivatives[23-25] in the presence of $AlCl_3$.

Polyphenylene-ethyl (PPE) is formed by polycondensation of 1,2-dichloroethane with benzene in the presence of $AlCl_3$. The molecular weight of PPE increases with decrease in the benzene: dichloroethane ratio and is maximal at the ratio 1.20 : 1,[26] but at 1.10 : 1 the only product of the reaction is insoluble PPE:



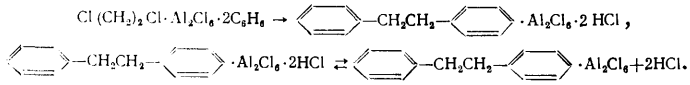
The first stage of the polycondensation of 1,2-dichloroethane with benzene in the presence of $AlCl_3$ is the formation of a complex of $AlCl_3$ with 1,2-dichloroethane[27]:

$$ClCH_2CH_2Cl + Al_2Cl_6 \rightleftarrows ClCH_2CH_2Cl \cdot Al_2Cl_6 .$$

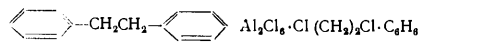
The complex reacts further with benzene, forming a ternary complex:

$$ClCH_2CH_2ClAl_2Cl_6 + 2C_6H_6 \rightleftarrows ClCH_2CH_2Cl \cdot Al_2Cl_6 \cdot 2C_6H_6 .$$

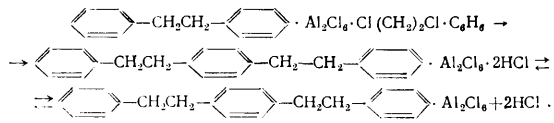
The reaction between 1,2-dichloroethane and benzene takes place inside this complex and leads to the formation of a diphenylethane–aluminium chloride–hydrogen chloride ternary complex.



The complex of diphenylethane and $AlCl_3$ reacts again with dichloroethane and benzene to form:



The reaction proceeds in the ternary complex and leads to the formation of a polymeric chain and the release of hydrogen chloride:



Further increase in the chain proceeds similarly. The yields of the reaction in the ternary complex were confirmed by Garmonov and coworkers[28] who isolated and determined the composition of this complex with the aid of labelled atoms. ^{14}C-Labelled benzene, toluene, ethylbenzene, propylbenzene, and 1,2-dibromoethane, were used.

The mixtures of the components deposited the complexes as dark red, heavy oily liquids. The change in the activity of ^{14}C-labelled radioactive specimens was measured with an end window Geiger counter. The results show that the ternary complexes have the composition:

$$HalCH_2CH_2Hal \cdot (5—7)\,ArR \cdot Al_2Cl_6 .$$

The composition of the complex is almost independent of the molar ratio of the components. Interestingly, with increase in the alkyl groups in the benzene ring the stability of the complex increases. A sufficient excess of one of the initial components is needed to shift the equilibrium

$$ClCH_2CH_2Cl \cdot Al_2Cl_6 + 2C_6H_6 \rightleftarrows ClCH_2CH_2Cl \cdot Al_2Cl_6 \cdot 2C_6H_6$$

to the right.

The polycondensation of aromatic hydrocarbons with dihalogenoalkanes in the presence of aluminium chloride is connected with their transfer from a hydrocarbon layer into a catalytic complex and back again. With this there is

a change in the value of the distribution of the hydrocarbons between the catalytic and hydrocarbon layers, just as in the alkylation of aromatic compounds[29].

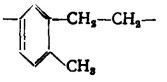
The reaction mass is a heterophase system consisting of a liquid catalytic complex of aluminium chloride with aromatic compounds, halogenoalkanes, and a hydrocarbon layer insoluble in the complex.

Poly(phenylene-ethyl) with a high molecular weight, 60 000, can be obtained by the polycondensation of diphenylethane[30,31]. To obtain a soluble polymer as well as increasing the temperature the reaction time must be shortened, otherwise a three-dimensional product is formed. To produce a high molecular weight the reaction must be stopped before the formation of a cross-linked polymer. An analysis of the infrared spectra of PPE obtained from dibenzyl and dichloroethane gives a basis for considering that a strongly cross-linked product is formed.

Poly(toluylene-ethyl) (PTE) is formed in the polycondensation of toluene with 1,2-dichloroethane[32]:

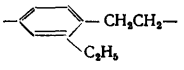
$$(n+1)\,C_6H_5CH_3 + n\,Cl\,[CH_2]_2Cl \xrightarrow{AlCl_3} CH_3C_6H_4\,[-CH_2CH_2C_6H_3(CH_3)-]_nH + 2HCl$$

The maximal molecular weight of PTE (4280) is reached when there is a slight excess of 1,2-dichloroethane and a cross-linked polymer is formed only when there is an excess of the latter. Steric hindrance is responsible for the difficulty in forming a cross-linked polymer. Destructive oxidation of the reaction products offers the possibility of suggesting the structure of the PTE chain:



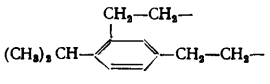
The infrared spectrum of the polymer also shows the presence of a 1,3,4-substituted nucleus in PTE.[33]

Yukel'son and coworkers[34] obtained poly(ethylphenylene-ethyl) (PEPE) by the polycondensation of ethylbenzene with 1,2-dichloroethane in the presence of $AlCl_3$. The highest molecular weight of PEPE is obtained at ethylbenzene : dichloroethane ratios close to 1. An analysis of the infrared spectra of the polymer shows that the benzene ring has predominantly 1,2,4-substitution:



The reaction of cumene with dichloroethane under the action of $AlCl_3$ gives poly(cumylene-ethyl) (PCE) with a low molecular weight even at a cumene : dichloroethane molar ratio[35].

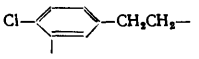
An analysis of the infrared spectrum of PCE shows that the main type of substitution of the benzene ring should be 1,2,4-substitution:



In polycondensation the isopropyl group is completely retained and n-propylbenzene is not formed under the action of $AlCl_3$. This is shown by an analysis of the NMR spectrum.

Shegoev[36] showed that the polycondensation of xylene with 1,2-dichloroethane proceeds smoothly and with a good yield of poly(dimethylphenylene-ethyl) (PDMPE), but in the polycondensation of di-isopropylbenzene with dichloroethane the process stops at the dimer stage owing to the large size of the alkyl substituents. However, the condensation of trialkylbenzene containing an alkyl with 1–3 carbon atoms and a dihalogenoalkane with 2–4 carbon atoms in the alkylene in the presence of $AlCl_3$ leads to the formation of a polymer with a molecular weight of 8000–9000.[37] The reaction of chlorobenzene with 1,2-dichloroethane gave poly(chlorophenylene-ethyl) (PCPE).[38] The greatest increase in the molecular weight to 4250 is observed in approaching an equimolecular ratio of the reactants and the formation of three-dimensional products at the equimolecular ratio. A 1% excess of chlorobenzene gives a mixture of a linear and a cross-linked product.

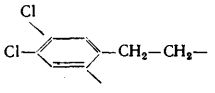
The study of the structure of PCPE by the method of destructive oxidation and an analysis of the infrared spectrum[39] suggests that the benzene ring of the chain is predominantly 1,2,4-substituted:



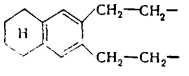
The formation of poly(fluorophenylene-ethyl) (PFPE)[40] proceeds similarly with the only difference that with a 5 mole % excess of fluorobenzene an exclusively three-dimensional infusible and insoluble polymer is formed. The molecular weight of the polymer reaches a maximum at a catalyst concentration of 6 mole % on the fluorobenzene and at a fluorobenzene : dichloroethane ratio of 1 : 1.19.

The PFPE unit cell has the same structure as PCPE.

Korshak and Kolesnikov[41] showed that increasing the substituents in the benzene ring still further hinders the formation of a cross-linked product. Thus in the polycondensation of 1,2-dichloroethane with *o*-dichlorobenzene in the presence of $AlCl_3$ (up to 6 mole %) insoluble products are not formed even when there is a considerable excess of dichloroethane. Poly(dichlorophenylene-ethyl) (PDCPE) of the highest molecular weight (~ 3920) is formed at the equimolecular ratio of the reactants. The polymer is a solid of low melting point (50 °C). Simultaneously with the polycondensation there is a redistribution of the halogen, leading to a decrease in the chlorine content of the reaction product. PDCPE consists mainly of monomeric units of the structure:



Insoluble products are also not formed during polycondensation of tetralin with 1,2-dichloroethane even with an excess of the latter[42]. Tetralin, like *o*-dichlorobenzene, can be regarded as a dialkyl derivative of benzene in which the substituents are in the *ortho*-position. The experimental results showed that the molecular weight of poly-tetralylene-ethyl (PTTE), which is a solid, rises to a maximum (6400) at the dichloroethane : tetraline ratio of 1 : 1.10. It is thought that in PTTE the tetralin residues are linked by $-CH_2-CH_2-$ groups, which occupy both β-positions in the aromatic ring of tetralin:

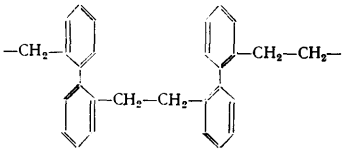


It is interesting to note that the molecular weight of PTTE remains constant in the range of catalyst concentrations 3–12 mole % of the tetralin.

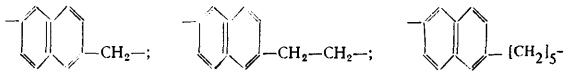
Poly(diphenylene-ethyl) (PDE) isobtained as a result of the reaction of biphenyl with dichloroethane[43,44].

A polymer with a molecular weight of 5120 is formed at a dichloroethane : biphenyl molar ratio of 1 and a catalyst concentration of 10 mole % of the biphenyl. At dichloroethane : biphenyl ratios > 1 and a catalyst concentration of

23 mole %, insoluble PDE is formed. Conclusions about the structure of the polymer are drawn on the basis of an analysis of the infrared spectra of PDE:



Polymers containing naphthalene rings in chains are also obtained under the same conditions:



Kolesnikov and coworkers[45] made copolymers in the dichloroethane–benzene–fluorobenzene and dichloroethane–chlorine–benzene–fluorobenzene systems. The ratio of the units $(-C_6H_4CH_2CH_2-):(-C_6H_3HalCH_2CH_2-)$ in the polymer obtained by common polycondensation of dichloroethane with benzene and fluorobenzene is less than in the copolymer obtained by the polycondensation of the dichloroethane–chlorobenzene–fluorobenzene system. This shows that the relative activity of fluorobenzene is less than the relative activity of chlorobenzene. The highest molecular weight of a copolymer of dichloroethane with benzene and fluorobenzene is 2610 and that of the copolymer of dichloroethane, benzene, and fluorobenzene is 2120. The rate of the polycondensation process in the dichloroethane–fluorobenzene–chlorobenzene system is appreciably greater than that in the dichloroethane–benzene–chlorobenzene system. The possibility of the synthesis of a ternary copolymer of dichloroethane with cumene and bibenzyl by polycondensation in the presence of $AlCl_3$ was shown by Kolesnikov and coworkers[46]. As expected, the molecular weight increases with the bibenzyl : cumene ratio.

It was found by turbidimetric titration that the polycondensation product is a copolymer and not a mixture of homopolymers. The infrared spectrum of the product of the common polycondensation of cumene and bibenzyl with dichloroethane is similar to that of PCE.

Hence from what has been stated above the following conclusions can be drawn:

1. In the polycondensation of either benzyl chloride or of aromatic hydrocarbons with halogenoalkanes in the presence of a Friedel–Crafts catalyst low-molecular-weight polymers are formed.

2. The highest molecular weight of polyarylenealkyls is reached on approaching the equimolecular dihalogenoalkyl : aromatic compound ratio, which agrees with the polycondensation theory.

3. Since the Friedel–Crafts catalyst is not stereospecific, the polyarylenealkyls obtained are branched and are a mixture of polymeric chains in which the benzene rings have different substitution.

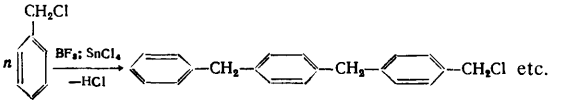
3. CHEMICAL REACTIONS OF POLY(ARYLENEALKYLS)

As a result of polycondensation polymers of low molecular weight and poor mechanical properties are formed. The polymers are either viscous liquids or solids difficult to reprocess. The polyarylenealkyls do not contain functional groups with the aid of which they could be subjected to chemical changes, whereas polyarylenealkyls such as PPM are thermally stable products and withstand heating in the absence of air to 380–400°C without undergoing significant changes[12].

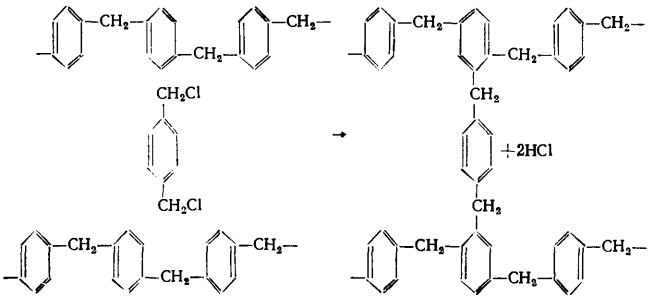
Polyarylenealkyls also exhibit increased resistance to radiation[47]. Thus the viscosity of lubricating oils of polymers obtained by the polycondensation of aromatic hydrocarbons $C_6H_{6-n}R_n$ (where R = alkyl C_1-C_5, $n = 1-5$) with alkylene dihalides C_1-C_4 (for example, $ClCH_2Cl$ or CH_2BrCH_2Br) in the presence of $AlCl_3$, $ZnCl_2$, or BF_3 after the action of a 2×10^9 rad dose of β-radiation increased by 150%, whereas ordinary mineral oil of the same viscosity showed an increase in viscosity of 500%.

A search is now being made for means of the chemical modification of polyarylenealkyls to obtain commercially usable products based on them.

Phillips[48] effected the cross-linking of polybenzyl with a Friedel–Crafts reaction. First the polycondensation of benzyl chloride in the presence of mild catalytic agents (BF_3 or $SnCl_4$) was brought about and fusible and soluble polybenzyl was obtained:



Cross-linking took place when this polymer reacted with *p*-dichloroxylene in the presence of a mild catalyst:



The products were named Friedel–Crafts polymers.

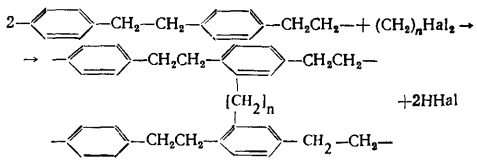
This method of cross-linking, proposed for strengthening polybenzyl and terphenyl, can also be used for other polymers which contain aromatic or heterocyclic rings.

Glass fibre, organic fibre, and siliconorganic fibres are readily impregnated by Friedel–Crafts polymers. The strengthening of these plastics is longer-lasting than, for example, with phenolic resins but the stability of these polymers to the action of chemical reagents is sufficiently high. Thus they do not have the drawback characteristic of phenolic resins—instability towards alkalis, since they do not contain hydroxyl groups arranged in series with methylene bridges. They are also stable to the action of radiation.

A little Friedel–Crafts catalyst is added to the polymer obtained from $\alpha\alpha'$-dichloro-*p*-xylene before moulding and during the moulding at 120–140°C a thermoreactive material which exhibits high thermal stability is formed[16].

The polymers which contain benzene rings in a chain separated by methylene groups, can be cross-linked also by dihalogenoalkanes in the presence of Friedel–Crafts catalysts. PPE with a molecular weight of 5900 was cross-linked with dihalogenoalkanes : methylene dibromide, 1,2-dibromoethane, 1-bromo-3-chloropropane, 1,4-dibromobutane, and 1,6-dibromohexane[49]. The dihalogenoalkanes can be arranged in the following series according

to the rate of formation of the trimer: 1,4-dibromobutane > 1-bromo-3-chloropropane > 1,6-dibromohexane > methylene dibromide > 1,2-dibromoethane. The cross-linking takes place in two stages. Initially a strongly branched polymer is formed, soluble up to a certain stage, and subsequently the branched molecules are converted into cross-linked ones and lose the ability to dissolve:



The higher the molecular weight of the initial polymer the less the need for a cross-linking agent. Initially the longer chains of the polymer molecules are cross-linked, which is shown by the drop in the molecular weight of the soluble part of the polymer.

Another method found for strengthening poly(arylenealkyls) is with the aid of sulphur[50]. In the reaction of poly(arylenealkyls) with sulphur at 200–250°C the sulphur is added to the polymer, hydrogen sulphide is eliminated, the viscosity increases, and double bonds are formed[51]. Most of the polymer becomes insoluble. The vulcanising of PPE, PTE, PEPE, PCE, PCPE, and PDE has been studied[52].

The controlling stage of the vulcanising of poly(arylenealkyls) is the breakdown of inactive sulphur particles into active ones.

The activation energy of the –S–S– bonds in the polysulphide chain of sulphur is 33.4 kcal mole^{-1} and the energy of the fission of $^{\bullet}S_2^{\bullet}$ to the monoradical is 63 kcal mole^{-1}.[53] The activation energy of the vulcanising of polyarylenealkyls lies in the range 37–41 kcal mole^{-1} [52] but the activation energy of the thermal destruction of poly(arylenealkyls)—for example, poly-(*p*-phenyleneethylene) has a value of not less than 58 kcal mole^{-1}.[54] On comparing the values given it can be assumed that the initial active species under the conditions of the reaction is $^{\bullet}S_2^{\bullet}$.

Owing to the formation of new chemical bonds between the poly(arylenealkyl) molecules structuring of the polymer takes place[55]. An analysis of the infrared spectra of vulcanised PPE, PTE, PEPE, and PCE prepolymers in the range of planar deformation vibrations (1225–960 cm^{-1}), of out-of-plane deformation vibrations (below 900 cm^{-1}), and also in the range of the overtones and constituent frequencies (2600–1650 cm^{-1}) shows the absence of changes in the substitution of the benzene ring of the chain[56].

On the basis of the above it has been suggested that in the thermal vulcanising of poly(arylenealkyls) cross-linking takes place by the loss of a hydrogen atom from the methylene groups of the bridge and the alkyl substituents. In the vulcanising of poly(arylenealkyls) owing to the dehydrogenating action of sulphur double bonds are formed conjugated with the benzene ring[57]. The electronic spectra of the vulcanised polymers show that sulphide bridges have the $-S_x-$ structure, where $x \geqslant 2$, and not of type =S= as suggested[58].

The vulcanising proceeds by a radical mechanism[57]:

$$S_8 \xrightarrow{>200^\circ} {}^{\bullet}S_y^{\bullet} + {}^{\bullet}S_z^{\bullet},$$

$$PH + {}^{\bullet}S_z^{\bullet} \rightarrow P^{\bullet} + HS_z^{\bullet},$$

$$HS_z^{\bullet} + HS_z^{\bullet} \rightarrow H_2S + {}^{\bullet}S_z^{\bullet},$$

$$P^{\bullet} + HS_z^{\bullet} \rightarrow PSSH,$$

$$PS_z^{\bullet} + PH \rightarrow PSSH + P^{\bullet},$$

$$P^{\bullet} + {}^{\bullet}S_z^{\bullet} \rightarrow PS_z^{\bullet},$$

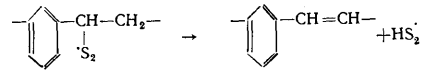
$$PSSH + PH \rightarrow PSP + H_2S,$$

$$PS_z^{\bullet} + PS_z^{\bullet} \rightarrow PS_4P,$$

$$P^{\bullet} + P^{\bullet} \rightarrow P-P,$$

where PH = poly(arenylalkyl).

The formation of double bonds evidently proceeds thus:



The appearance of absorption bands in the 970–960 cm^{-1} range in the infrared spectra shows the presence of double bonds. After bromination of the poly(alkylenealkyl) this absorption band is not present in the infrared spectrum.

The radical nature of the interaction of sulphur with poly(arylenealkyls) is confirmed by the fact that the products of the thermal vulcanising, subjected to EPR analysis, show a narrow absorption line (~ 10.0e) without signs of hyperfine structure with a *g*-factor of the free electron[59]. The concentration of the paramagnetic species for the vulcanised prepolymers of PPE, PTE, PEPE, PCPE, and PCE falls within the range $(0.12-0.5) \times 10^{20}$ g^{-1}. The EPR signal is unchanged after the products have been stored for several months, but in dissolution in toluene it disappears and does not reappear after removal of the solvent. The intensity of the EPR signal is also reduced on irradiation of the specimens with X-rays. The existence of an EPR signal in vulcanised poly(arylenealkyls) is due to the formation of radicals of the type $R_{arom}-CH_2-\dot{C}H-R_{arom}$ and $R_{arom}-\dot{C}H_2$ produced according to the scheme given above.

Poly(arylenealkyls) react with sulphur at different rates[60]. They are arranged according to hydrogen sulphide liberation in the order PDE > PCE > PTE > PEPE > PCPE and according to the rate of formation of a cross-linked polymer in the order PEPE > PPE > PTE > PCE > PCPE > PDE. Such a difference in the rate of liberation of hydrogen sulphide and the formation of a cross-linked polymer depend on the structure of the initial poly(arylenealkyl). The activating action of the benzene ring on the methylene groups of the bridge ensures that PDE has a high rate of reaction with sulphur. The presence in the benzene ring of the electronegative substituent chlorine reduces the lability of the hydrogen atoms of the methylene groups in the *o*-position to chlorine. Therefore the vulcanisation of PCPE takes place under more severe conditions.

The high rate of gelatinisation for PEPE ensures the presence of a methylene group at the substituent $-CH_2CH_2-$ which should react just like the bridge methylene groups.

The vulcanised poly(arylenealkyls), prepolymers, are solids soluble in aromatic hydrocarbons and halogenoalkanes. Subsequent heating of the prepolymers at temperatures not less than 200°C leads to the formation of cross-linked products.

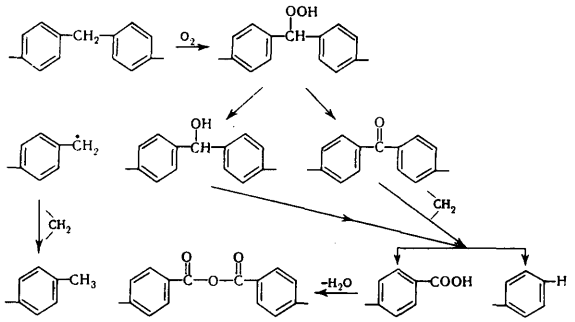
Vulcanised poly(arylenealkyls) can be used as thermoreactive paint constituents[57]. Coatings based on such polymers exhibit good dielectric properties, high chemical stability, and good adhesion to metals.

The prepolymers can be used also as binding agents for plastics, for which purpose glass fibre is impregnated with the prepolymer, pressed and hardened at 220°C or above. The specimens exhibit good thermal stability and chemical resistance and have physico-mechanical indices higher than for plastics based on phenol–formaldehyde resins.

Vulcanised poly(arylenealkyls) have a stabilising effect, like low-molecular-weight antioxidants of the R–S–S–R type[61].

To reduce the temperature of structuring of the poly-(alkylenealkyls) with sulphur, vulcanising under the action of aluminium chloride was studied[62]. The reaction takes place at 80–90°C. Unlike thermal vulcanising, the formation of new chemical bonds in the polymer evidently occurs at the benzene ring. The structured polymer formed in the catalytic vulcanising is a powdery product but the cross-linked polymer after thermal vulcanising is a tough material, ground into powder with difficulty.

Conley[63] studied the thermal oxidation of polybenzyl in air and in oxygen in the temperature range 140–220°C and proposed a mechanism for the oxidation:

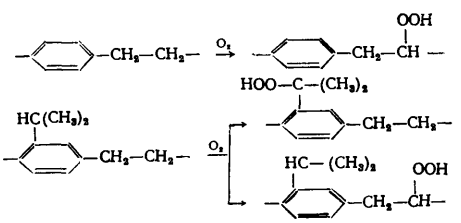


The oxidation, like the vulcanising, takes place at the methylene bridges with the formation of ketonic and carbonyl groups. On the basis of the results on the rate of formation of carbonyl compounds, the initial activation energy of the oxidation was found to be 14.5 ± 3.5 kcal. A vapour-phase chromatographic analysis of the volatile products shows that the main products of the oxidation are benzoic acid and benzophenone; small amounts of toluene, water, and CO_2 are formed. The secondary reactions of the decomposition, which lead to breaking of the chain are considered to be further oxidation of the benzhydrilic and benzophenone bonds.

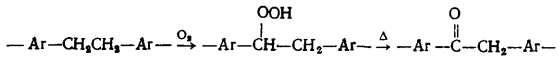
The thermal oxidation of several polymers containing a chain of benzene rings separated by two methylene groups has been studied. It was found that unlike polybenzyl and poly-(*p*,*p*'-diphenylenemethylene) appreciable decomposition of most of the polymers with a $-CH_2-CH_2-$ bond in oxygen is observed in the temperature range 340–410°C.[1] These polymers can be arranged in the following order of thermal oxidation resistance: poly-(2,6-naphthylene-ethylene) > poly-(*p*-phenylene-ethylene) > poly-(9,10-anthrylene-ethylene).

The mechanism given for the oxidation of polybenzyl is evidently correct for the thermal decomposition of these polymers.

Kolesnikov and Chuchin[64,65] oxidised several poly-(arylenealkyls) both in the melt and in solution. The oxidation as far as hydroperoxides proceeds according to the scheme:



An analysis of the infrared spectra showed that the oxidation of poly(arylenealkyls) in the melt goes further than in solution. The spectrum of poly(cumylene-ethyl) oxidised in the melt gave absorption bands characteristic for aromatic acids (1270 cm^{-1}), aldehydes (1715 cm^{-1}), and other oxygen-containing groups. In the oxidation of poly-(arylenealkyls) in cumene the decomposition products of the hydroperoxides do not contain tertiary alcoholic groups. In thermal decomposition poly(phenylene-ethyl) hydroperoxide gives the same products as poly(cumulene-ethyl) hydroperoxide, obtained by oxidation in cumene. Judging by the infrared spectra, the hydroperoxides have the same structure, that is, the oxidation takes place at the methylene groups just as in the thermal oxidation of polybenzyl[63] and the thermal destruction of poly-(*p*-xylylene).[66] The decomposition follows the reaction:



The oxidation of PPE in cumene and tetralin solutions was studied and it was found that the oxidation in cumene is much faster than that in tetralin[67]. Analysis of the infrared spectra showed that oxidation of PPE by atmospheric oxygen at elevated temperatures proceeds like oxidation by oxygen at 80°C, mainly to the hydroperoxide.

Poly(cumylene-ethyl) (M = 1100) oxidised by oxygen in the presence of benzoyl peroxide gave a polymeric hydroperoxide containing 2.4% hydroperoxide groups.

The decomposition of the hydroperoxides is a first-order reaction with an activation energy of 3.5 kcal $mole^{-1}$.

The product of the common polycondensation of cumene and dibenzyl was oxidised[69] and it was found that with increase in the fraction of cumene in this reaction mixture the concentration of peroxide groups in the oxidised poly-(arylene-ethyl) increases, reaching a maximal value in PCE. The reverse picture was observed in the oxidation of poly(arylenealkyls) in cumene solution, when the maximal concentration of hydroperoxide groups was observed in the oxidation of PPE. This difference has been explained[69] by the presence of an alkyl substituent in the benzene ring, which weakens the induction effect, in connection with which there is a decrease in the mobility of the hydrogen atom of the methylene group. Therefore in the common presence in the benzene ring of methylene groups and of groups with α-carbon tertiary atoms a decrease in the rate of autoxidation of dialkylbenzenes and a decrease in the maximal concentration of hydroperoxide was observed. This evidently also explains the increase in the concentration of hydroperoxide groups in poly-(arylene-ethyl) with decrease in the proportion of isopropyl groups in the polymeric chain.

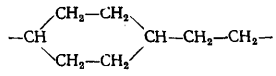
The polymeric hydroperoxides synthesised were used for the production of ion-exchange resins.

Granular sulphonic cation-exchange resins were obtained on the basis of spatially cross-linked copolymers, by the adding on of styrene to polymeric hydroperoxides[70]. For the chain carrier and polymeric initiator respectively the polyarylenealkyl (a product of the common polymerisation of cumene and bibenzyl with dichloroethane) and its hydroperoxide were used; divinylbenzene was the cross-linking agent.

The capacity of the ion-exchange resins, determined by the degree of vulcanising of the specimens, increases with increase in the proportion of poly(arylenealkyl) in the original mixture and of hydroperoxide groups in the polymeric hydroperoxide.

The sulphonic cation-exchange resins obtained are capable of sorbing large organic ions[71].

Poly(arylenealkyls) were subjected to hydrogenation[72], as a result of which poly(cycloalkylenealkyls) of the general formula

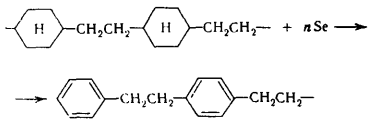


were obtained. The hydrogenation was carried out in the presence of a solvent and in a melt on Raney nickel, according to the reaction:

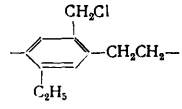
$$[-CH_2-CH_2C_6H_4-]_n + 3n\,H_2 \xrightarrow{Ni} [CH_2-CH_2-C_6H_{10}-]_n$$

The hydrogenation products of the poly(arylenealkyls) retain their initial appearance but their colour is appreciably paler than that of the original polymers. The molecular weight of the hydrogenated poly(arylenealkyls) is almost the same as that of the original polymer.

Dehydrogenation of the hydrogenated PPE with selenium led to the initial poly(phenylethyl):



Polyarylenealkyls are readily chloromethylated. The chloromethylation of PEPE[71,73] gave the polymer



containing up to 19% chlorine.

Water-soluble polyelectrolytes were obtained by the same method. To do this, first the PPE was chloromethylated, then the product was aminated, or vulcanised, or phosphorylated; this was followed by hydrolysis and oxidation[74].

Yukel'son and coworkers[75] nitrated poly(arylenealkyls) and obtained nitro-products with up to 6% free nitrogen. The use of nitropolymers as plasticizers and antioxidants in rubber mixtures based on SKS-30 ARKM rubbers increases the strength properties of the vulcanised products.

Hence the following conclusions can now be drawn:

1. For the improvement of the physicomechanical properties of poly(arylenealkyls) obtainable by polycondensation, several methods for strengthening them have been found.

2. The low melting point and good solubility of the polymers isolated at intermediate stages of the process enables these polymers to be treated rather simply.

3. The introduction of functional groups in poly(arylenealkyls) opens paths for their use for practical purposes.

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Voronezh Technological Institute

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Biologically Active Compounds of Silicon

M.G.Voronkov and E.Lukevics

The literature data and the studies by the authors of the review on biologically active organosilicon compounds are reviewed. The role of silicon in living organisms, the toxicity and biological activity of its organic derivatives, and the therapeutic applications of its compounds are discussed.
The bibliography includes 358 references.

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1. INTRODUCTION

The unusually wide practical applications of inorganic and organic compounds of silicon resulting in daily and frequently direct contact with the human organism, the increasing use of organosilicon polymers in medicine, cosmetics, and the food industry, and also the continued contact of all living terrestial organisms with natural silicon compounds led to the widely held view that this element is biologically inert. Silicon does not belong either to macro- or oligo-biogenic elements [1] and it is usually believed that it does not play an appreciable role in the vital processes of higher animals and man. However, in reality this is not the case.

Silicon compounds play a significant role in vital processes and many of them (particularly organic derivatives) have specific effects on living organisms.

The present paper, which is based on the plenary report by one of the authors (L. G. Voronkov) at the Second International Symposium on the Chemistry of Organic Silicon Compounds in Bordeaux (July, 1968), is a brief review of studies devoted to the elucidation of the role of silicon in living organisms and in particular the biological activity of organosilicon compounds. Its aim is to draw the attention of specialists in the field of organosilicon chemistry, biochemists, biologists, pharmacologists, and physicians to a new and extremely interesting and important branch of the chemistry of silicon.

2. THE ROLE OF SILICON IN LIVING ORGANISMS

The scientific data accumulated so far leave no room for doubt that silicon is one of the principal elements and not only in non-living nature. About 10 000 million tons of silicon are involved in the life cycle of living matter on our planet [2]! This element is included (albeit in slight amounts) in the composition of all plant and animal organisms and their existence without it is impossible [2-23].

Silicon compounds play a particularly important role for many living entities at a lower stage of evolutionary development (silicate bacteria, the simplest algae, spore plants, etc.) in whose organisms it is present in very large amounts [23-54]. Silicon is also important for many higher plants, which have come to be called "siliceous" because of their high silicon content. Silicon compounds play extremely important functions also in the organisms of higher animals and man, despite the fact that in the majority of their organs the content of this element is relatively small. In the tissues of human and animal organisms silicon compounds are present in three principal forms [14,55-76].

1. Water-soluble inorganic compounds capable of passing through cell walls which can be readily eliminated from the organism. These include orthosilic acid and ortho- and oligo-silicate ions.

2. Organosilicon compounds and complexes soluble in organic solvents and containing Si–O–C groups. These include ortho- and oligo-silicate ethers derived from carbohydrates, proteins, cholesterol and other steroids, choline, lipids, and phospholipids. Compounds containing Si–N–C bonds may also be present. Organosilicon compounds containing Si–C bonds have not been detected in higher animal and human organisms but they have been found in the bacteria *Proteus Mirabilis* [29,31].

3. Insoluble silico-polymers. These include polysilicic acid, amorphous silica, and insoluble silicates and quartz. In the organism the surface of these polymers is always covered by a chemisorbed layer of organic compounds containing hydroxy- or amino-groups.

It has now been firmly established that silicon compounds are essential for epithelial and connective tissues to which they impart, in particular, strength, elasticity, and impermeability. It is also suggested that silicon compounds play an important role in all metabolic processes in living matter, in particular in the metabolism of lipids. They probably participate in the dynamics of living plasma, their role consisting in altering the surface potential of cells. It is suggested that silicon compounds also participate in oxidation processes and enter into the composition of diastases as a coenzyme.

Thus the presence of silicon compounds in organisms is not only normal but necessary. Furthermore, living tissues exhibit a definite affinity for silic acid ("silicotropism"). The metabolism of silicon compounds in the cells of the organisms is evidently determined by the activity of special enzymes.

Numerous pathological processes, including cancer, atherosclerosis, tuberculosis, and diabetes, goitre, certain types of dermatitis, stone formation in the urethra, etc., are associated with the breakdown of the metabolism of silicon compounds. The latter play an important protective role in the organism, improving its self-protective functions and the capacity for detoxication. Partly this is due to the fact that silicon compounds facilitate the removal with urine of metabolites and extraneous and toxic substances, serve as a barrier preventing the propagation of degenerative processes [13], and intensify the biosynthesis of collagen [77].

3. THERAPEUTIC APPLICATIONS OF SILICON COMPOUNDS

Bearing in mind the important role of silicon in the normal activity of the organism, one may hope that the regulation of its metabolism by the introduction into or the removal from the organism of definite compounds of this element will lead to considerable advances in the treatment of many diseases and in the fight against old age. The first attempts on these lines were made long ago although they were not always entirely successful. Their inadequate effectiveness can be explained by the extremely narrow range and lack of variety of the silicon compounds used in the attempt at therapy (silic acid, silicates of sodium, potassium, cobalt, magnesium, iron, and copper, kaolin, and talc) [78-109]. All these inorganic compounds are insoluble or give rise to the insoluble silic acid on contact with gastric juices and therefore they are assimilated by the organism with difficulty.

At the same time mineral waters rich in soluble compounds (containing 20–80 mg litre^{-1} of silica) are distinguished by high physiological activity and have been used for a long time in treatment at spas [110]. They exhibit sympathomimetic activity, have a favourable effect on cardiac muscle, sharply intensify cardiac activity and heart rhythm, inhibit the motor function of the small intestine, intensify the capacity for work of skeletal muscle, greatly intensify the activity of the ciliary epithelium of the alimentary canal, etc. Mineral waters rich in silicon content not only improve the positive silicon balance in the organism but also significantly alter the functional state of the liver, the stomach, and the kidneys. They intensify the activity of the oxidative enzymes in the liver, increase the content of adrenaline in the adrenal glands and the content of noradrenaline and the oxidation products of aminocatechols in cardiac muscle, and have a favourable effect on the autonomic nervous system. Silicate mineral waters are widely used in the therapy of uric acid diathesis, inflammatory diseases of the urinogenital system, etc.

In the first half of the present century tuberculosis and certain other diseases began to be treated by various orthosilicate esters. These include, in particular, the preparation "Silistren" produced by the Bayer company, which consists of the tetraglycol ester of orthosilic acid [111-117]. Orthosilicate esters of hydroxycarboxylic acids and their esters and salts have also been used [118-123]. Other organic derivatives of orthosilicic [84,124-129] and even fluorosilic acid [130,131] have been proposed for use in therapy. Inorganic silicon compounds were not forgotten either. Quite recently the resistance of guinea pigs to tubercular infection was found to increase after peroral introduction of sodium silicate [132-134].

Using these and similar preparations, specialists in therapy assumed that the therapeutic effect of silicon compounds in tuberculosis consists in the stabilisation of lung tissue and in the formation of a protective coating in the affected region [78,85,89].

One of the rational approaches to the problem of "silicon therapy" consists in the use for therapeutic purposes of "plant silicon" present in plants, for example in the horse-tail [13,94,135-141]. In these plants silicon is present to a large extent as organic compounds [142] already incorporated in cellular protoplasm. Silicon compounds of precisely this type are in fact assimilated by man together with food, but, according to Monceaux [13], the human organism cannot assimilate inorganic silicon compounds in the way that autotrophic plants can.

Complexes of potassium methylsilicate [Me Si(OH)(OK)$_2$ (Ed. of Translation)] with salicylic, citric, ascorbic, heparinic, penicillic, or deoxyribonucleic acids have been proposed for the treatment of acute and chronic diseases of the joints, supercutaneous staphylococcal diseases, hypertension, sclerosis, various types of arteritis of the lower limbs, diseases of the capillaries, atrophic phenomena, the breakdown of cellular mitosis, and a number of other affections [143]. The use of silicon compounds in the treatment of atherosclerosis proved to be particularly successful. In this disease the silicon content in the tissues of the arteries is known to decrease sharply [144-150]. The introduction of sodium silicate [148], phenylpolysiloxane [151], and the complexes of potassium or sodium methylsiliconate with salicylic [150] or citric acids [143,152] not only prevents the occurrence of experimental atherosclerosis but also has a therapeutic effect.

In view of the particular ease of penetration of the complexes of potassium methylsilicate with organic acids into the organism via the skin [153], their anti-inflammatory and antisclerotic activity, and also the stimulating effect of silicon on the synthesis of connective and elastic tissues [149], an effective method has been developed for the treatment of coronary affections based on the use of controlled ionophoresis [154,155]. Ionotherapy using complexes of potassium methylsilicate with citric or heparinic acids is used at present in the treatment of chronic heart disease (including treatment after 1–2 myocardial infarctions), arterial hypertension, and obliterative arteriopathy of the lower limbs. A seven year clinical experiment with 500 patients resulted in 80% of complete cures [154,155].

Complexes of potassium methylsilicate with organic acids have also been used in the treatment of cancer: cancer of the bone (osteosarcoma), the lungs, and the prostate gland. According to Janet [156], in many cases, in particular in the treatment of rapidly evolving tumours, satisfactory results have been achieved.

The complex of potassium methylsilicate with penicillin G proved to be effective in the treatment of myxomatosis, a virus disease which is not affected either by potassium methylsilicate or penicillin G used separately [157]. Thus the use of the complex with potassium methylsiliconate extended the spectrum of activity of penicillin. This could also prove true of other antibiotics.

A special application of organosilicon compounds in medicine [158-168] consists in the increasing use of polyorganosiloxane liquids, resins, and rubbers in the therapy of the diseases of the stomach, eyes, and the respiratory tract, in surgery, haemotology, dermatology, dentistry, and vetinary practice. However, in this case their application is based mainly on the specific physical properties of the organosilicon polymers (hydrophobic, antiadhesive, and antifoaming effects, etc.), their high chemical stability, and high physiological inertness.

4. TOXICITY OF ORGANOSILICON COMPOUNDS

The vigorous development of the organic chemistry of silicon after the Second World War led to the creation of a wide range of organosilicon polymers and materials based on them. At present the number of known individual organic silicon compounds exceeds 15 000. The outstanding practical importance acquired by organosilicon polymeric compounds made it necessary, of course, to investigate their physiological activity and in the first place toxicity. However, the range of compounds investigated in this respect remained very narrow until recently, being largely restricted to products of industrial synthesis (alkoxysilanes [189-224], chlorosilanes, [12,23,192,195-199,202,204,206,207,212,216,221,222,225-253] and polyorganosiloxanes [174-177,200,205,254-286]). The toxicity of other classes of organosilicon compounds, in particular nitrogen-containing compounds, has been investigated very little [191,194,198,203,209,213-215,217,223,224,287-304].

No organosilicon compound with a particularly distinct or specific physiological activity closely related to the presence of a silicon atom in the molecule had been found until the beginning of systematic studies by the present authors (1962), although fairly toxic (lethal dose LD_{50} = 1–50 mg kg^{-1}) compounds with $Si-OCH_2CH_2$, [305] Si–F, [306-310] and Si–NC [254] bonds have been synthesised. However, the effect of such compounds with silicon-containing functional groups on the organism is largely due to the toxicity of their hydrolysis products ($HOCH_2CH_2F$, HF, HCN).

Table 1. Toxicity of $(CH_3)_{4-n}SiX_n$.

X	References	Test animals	Method of administration	Characteristics of toxicity	h = 1	2	3	4
Cl	222	white mice	by inhalation	LC^*_{100}	0.1	0.4	0.4	15
OC_2H_5	199	rats	oral	LD_{100}	2	10	10	5
$OCH_2CH_2NH_2$	295	white mice	intraperitoneal	LD_{50}	0.32	0.57	0.40	—
$OCH_2CH_2N(C_2H_5)_2$	295	white mice	intraperitoneal	LD_{50}	0.50	0.72	0.60	0.23

*LC = absolute lethal concentration (mg litre^{-1}); LD = lethal dose (g kg^{-1}).

Nevertheless it can be asserted that the specific effect of the silicon atoms in the molecule of more or less readily hydrolysable compounds with silicon-containing functional groups in the series $R_{4-n}SiX_n$ does affect their toxicity. Firstly, the toxicity of such substances often proves to be appreciably higher or lower than that of their hydrolysis products used separately. This is clearly seen, in particular, for tetramethoxysilane [193-194], which is more poisonous and dangerous than methyl alcohol and colloidal silicic acid. Secondly it would appear that the toxicity of compounds of this type should increase with the number n of functional groups at the silicon atom, since this involves an increase in the amount of toxic agent formed in the organism on hydrolysis:

$$R_{4-n}SiX_n + n\,H_2O \rightarrow R_{4-n}Si(OH)_n + n\,HX \quad (n = 1-4).$$

However, silicon compounds with $n = 1$, i.e. the least hydrolysable compounds forming on hydrolysis a minimal amount of HX, proved unexpectedly to be the most toxic (Table 1).

In this connection it should be noted that in the series of organotin compounds $R_{4-n}SnX_n$ the monofunctional compounds ($n = 1$) are also the most toxic [311].

5. BIOLOGICAL ACTIVITY OF ORGANOSILICON COMPOUNDS

The aim of the first attempts to prepare physiologically active organic compounds of silicon was the synthesis of silicon analogues or organosilicon derivatives of organic substances known to have a pronounced and definite effect on the organism. In the course of studies of this kind the biological activity of a fairly large range of organosilicon compounds, described in Table 2, was investigated.

Table 2. Compilation of studies on biologically active organosilicon compounds.

Type of Effect	Compounds investigated
1	2
Effect on respiratory activity	*N*-trimethylsilylpyrrolidone [312], triethylisocyanatosilane [313], silatranes [22, 287-293], 2-aminoethoxysilanes [293, 295], 3-aminopropylsilanes [293,294,298], organosilicon arylalkylamines [301, 314], barbiturates [302, 315], carbamates [23, 300, 303, 304], aromatic acid amides [316]
Anabolic, androgenic, and oestrogenic activity	Organosilicon derivatives of steroids [317-319]
Allergic reactions	Dis(hydroxyphenyl)dialkylsilanes [320]
Inhibition of dihydronicotinamide adenine dinucleotide ($NADH_2$)-oxidase	Organosilicon carbamates [23]
Cholinergic and anticholinergic activity	2-(trimethylsilyl)ethyl acetate [321], 2-(dialkylamino)ethyl esters of trialkylsilylphenyl-β-hydroxypropionic acids [322], organosilicon carbamates [323], organosilicon derivates of choline [299]
Insecticidal activity	Organoisothiocyanatosilanes [324], polyorganosilthianes [325], organosilicon derivatives and analogues of pyrrolidone [312], sulphonamides [326], carbamates [327], salts of dithiocarbamic acids [328], unsaturated diols [329], and DDT [330], trialkylsilylalkyl phosphonic acid esters [331], organosilicon derivatives acetylene [332], trialkyl(trialkylsiloxy)stannanes [333]
Insect repellent activity	Methyl (*NN*-dialkylaminomethyl)dialkoxysilanes [334, 335], *N*-(trialkylsilylmethyl)-ethylamides of carboxylic acids [336]
Fungistatic activity	Organosilicon amines [293, 314, 337], organoisothiocyanatosilanes [324], polyorganosilthianes [325], organosilicon derivatives of mercury [338, 339], copper salts of dithiocarbamic acids [328], sulphonamides [326], and isothiocynates [340]
Bacteriostatic activity	3-Aminopropylsilanes and other organosilicon amines [293, 314, 337, 341], bis(hydroxyphenyl)-dialkylsilanes [342], trimethylsilylmethanol [343], mercury-containing polyorganosiloxanes [338], organosilicon derivatives of penicillin [344, 345], alkyl esters of aziridinecarboxylic acids [346]; and 2-(dialkylamino)ethyl esters of aromatic acids [347], organoethynylsilanes [348]
Regulation of plant growth	Chloroalkylsilanes [349, 350], ethynylsilanes [351]

Of the pharmocologically investigated [299] organosilicon derivatives of physiologically active organic compounds synthesised in our laboratory [352], mention should be made of the previously unknown *C*- and *O*-trialkylsilyl derivatives

of choline—$[R_3SiCH_2NR'R''CH_2CH_2X]Y$ and correspondingly $[(CH_3)_3NCH_2CH_2OSiR_3]Y$ (Table 3).

All compounds of this type exhibit *N*-cholinolytic activity. In this respect the most active compounds exhibit also ganglion-blocking activity on the parasympathetic ganglia of the heart. The hypotensive effect of organosilicon derivatives of choline is particularly pronounced for *C*-silyl substituted derivatives with R = R′ = R″ = CH_3 and Y = I in which the substituent X is the $OCOCH_3$ group (70–90 mmHg at a dose of 1 mg kg^{-1}) or an iodine atom (50–60 mmHg). Apart from the depressor response, these compounds cause intensified respiration in cats.

Table 3. Biological activity of organosilicon derivatives of choline.

Compound	Cholinolytic activity (straight muscle of frog stomach) EC_{50}^{*}	Ganglion-blocking activity (in cats) ED_{30} mg kg^{-1}	Hypotensive activity (in cats) ED_{30} mg kg^{-1}	Median lethal dose (for white mice with intraperitoneal administration) LD_{50}, mg kg^{-1}
$[(CH_3)_3SiCH_2N(CH_3)_2CH_2CH_2OH]I$	$8.0\cdot10^{-4}$	0.56	2.5	266
$[(C_2H_5)_3SiCH_2N(CH_3)_2CH_2CH_2OH]I$	$4.9\cdot10^{-4}$	0.85	3.6	53
$[(CH_3)_3SiCH_2N(CH_3)_2CH_2CH_2Cl]I$	$9.1\cdot10^{-5}$	0.50	0.86	124
$[CH_3(C_2H_5)_2SiCH_2N(CH_3)_2CH_2CH_2Cl]I$	$3.2\cdot10^{-4}$	0.35	1.69	71
$[(CH_3)_3SiCH_2N(CH_3)_2CH_2CH_2I]I$	$2.5\cdot10^{-5}$	0.69	0.25	40
$[(CH_3)_3SiCH_2N(CH_3)_2CH_2CH_2OCOCH_3]I$	$2.4\cdot10^{-4}$	0.62	0.7	328
$[(CH_3)_3SiCH_2N(CH_3)_2CH_2CH_2OCOC_6H_5]I$	$2.3\cdot10^{-5}$	1.26	3.1	465
$[(CH_3)_3SiOCH_2CH_2N(CH_3)_2]I$	$4.5\cdot10^{-4}$	—	—	238
$[(CH_3)_3SiCH_2NH(CH_3)CH_2CH_2Cl]Cl$	$1.3\cdot10^{-5}$	—	—	137

*Concentration expressed in fractional units.

The trimethylsilyl ester of choline has virtually no ganglion-blocking activity. When administered to cats in doses of 2–10 mg kg^{-1} the depressor phase is replaced by a pronounced increase in the level of blood pressure. The persistence of the pressor effect in experiments on spinal cats after the vagus nerves have been severed, the exclusion of the adrenal glands from blood circulation, and the prevention of this effect by hexamethonium salts indicate a stimulating effect of the trimethylsilyl ester of choline on the autonomic vegetative ganglia, particularly the sympathetic ganglia.

The physiological activity of organosilicon derivatives or analogues of known organic medicinal preparations and other substances with a distinct biological activity is not by itself in any way surprising. Although among all the compounds of this type investigated none has found wide practical application, investigations in this field are nevertheless very interesting and promising. This claim is based on studies of the "bioisosteric" organosilicon compounds carried out in recent years in the USA by Fessenden [23,300–304,353]. The idea underlying them may be regarded as the pharmacochemical development of the once very popular "analogue hypothesis" of Wöhler, Ladenburg, and Friedel, according to which the replacement in any organic compound of one or several carbon atoms by silicon (i.e. the formation of a "sila-derivative") does not alter appreciably the physical and chemical properties. Although this hypothesis has now been disproved, it nevertheless remains to a certain degree valid when applied to organosilicon compounds which do not contain functional groups attached to the silicon atom, at any rate functional groups which are readily hydrolysed.

As an example of the validity of the analogue hypothesis for carbon and silicon compounds in its pharmocological aspect, several pairs of isostructural substances are quoted below:

$(4\text{-}HOC_6H_4)_3M(CH_3)_3$ (I) $\quad C_6H_5(CH_3)_2MCH(CH_3)NH_2\cdot HCl$ (II)

$R(CH_3)_2M(CH_2)_nOCONH_2$ (III) $\quad R(CH_3)M[(CH_2)_nOCONH_2]CH_2OCONH_2$, (IV)

where M = C (a) or Si (b).

Thus compounds (Ia) and (Ib) exhibit the same allergic activity [320]. The organosilicon analogue (IIb) of the familiar adrenergic medicinal preparation (IIa) resembles it in both its overall biological activity and in its toxicity [301]. The toxicity of organic carbamates (IIIa, IVa) and the organosilicon carbamates having an analogous structure (IIIb, IVb) is of the same order of magnitude [303].

The similarity of the biological activities of isostructural organic and organosilicon compounds is of undoubted interest for the creation of new medicinal preparations, pesticides, and other types of biologically active substances if only because the corresponding silicon compounds are in many cases easier to synthesise and are cheaper. Nevertheless sometimes the sila-analogues of the physiologically active organic substances may differ from the latter to a greater or smaller extent in their effect on the organism. In turn this difference may be successfully used in the synthesis of new medicinal preparations and pesticides.

For example the familiar tranquiliser meprobamate (Va) and its sila-derivative (Vb), [303]

$CH_3CH_2CH_2(CH_3)M(CH_2OCONH_2)_2$ (V)

where M = C (a) or Si (b), has similar effects on the motor activity of animals and inhibits NAD-H_2 oxidase. However, their physiological activity is otherwise not the same. The effect of compound (Va) is four times more prolonged than that of (Vb). When administered orally, compound (Vb), in contrast to compound (Va), is inactive despite the fact that it is absorbed and then eliminated from the organism in urine. This suggests that the metabolic fate of both analogues (V) in the organism is different. Indeed, while compound (Va) is oxidised in the organism and eliminated as the hydroxy-derivative (VIa), compound (Vb), apart from being oxidised by an analogous process to compound (VIb), is converted into the disiloxane (VII) with elimination of an n-propyl group [23,353]:

$CH_3CH(OH)CH_2(CH_3)M(CH_2OCONH_2)_2$ [VI; M = C (a); Si (б)] $\quad [CH_3(H_2NCOOCH_2)_2Si]_2O$ (VII)

The only metabolic product of $CH_3CH_2CH_2(CH_3)_2SiCH_2OCONH_2$ is the corresponding dealkylation product $[H_2NCOOCH_2(CH_3)_2Si]_2O$†. [353] Thus the different metabolic fate of the sila-analogues of physiologically active substances may have a significant effect on the nature and duration of their action.

The carbon and silicon structural analogues of type (VIII) show particularly marked differences in their biological activity, which can probably be attributed to the β-effect of the silicon atom:

$(CH_3)_3MCH_2CH_2OCONH_2$ (VIII)

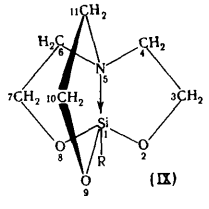
where M = C (a) or Si (b).

†Until Fesenden's investigation [353], the metabolism of organosilicon compounds in the organism was hardly studied. It was only known that $(CH_3)_3Si(CH_2)_{15}CH_3$ and $(CH_3)_3Si(CH_2)_{11}COOCH_3$ are absorbed via the gastrointestinal tract [354] and that [^{14}C] polydimethylsiloxane is not eliminated from the organism in the form of $^{14}CO_2$. [355]

Compound (VIIIa) is ten times more toxic than its sila-analogue (VIIIb). The latter is a rapid-acting muscle relaxant which does not give rise to side effects. On the other hand, compound (VIIIa) does not exhibit this type of activity, causing convulsions instead [303]. At the same time both compounds (VIII) give rise to a prolonged cholinergic response when introduced into the lateral hypothalamic region of the brain [356].

The last few examples clearly demonstrate that in physiological activity too the "analogue hypothesis" is not always justified even when compounds with silicon-containing functional groups are excluded from consideration. This is not in fact surprising because the much lower electronegativity, the higher covalent radius of the atom (by a factor of 1.5), and the presence of vacant 3*d* orbitals constitute appreciable differences between silicon and carbon. This difference does actually lead to the expectation in a number of cases that the sila-analogues of physiologically active organic compounds will have a quite specific effect on living organisms. This makes further investigations in this field undoubtedly promising.

We believe that even more interesting and promising is the study of the physiological activity of organosilicon compounds which have no organic analogues at all or which exhibit an activity which is closely related to the presence in their molecule of a silicon atom (or atoms). Compounds of this type, investigated up to the present time, are also listed in Table 2. These include in the first place silatranes (IX), the wide employment of which in our laboratory began in 1962. We have shown that certain silatranes, namely 1-arylsilatranes exhibit high and specific physiological activity [22,287-293,357].



(IX)

For example, 1-phenylsilatrane (IX, R = C_6H_5) and even more so 1-*p*-tolylsilatrane (R = *p*-$CH_3C_6H_4$) are unusually toxic for warm-blooded animals. Their lethal dose (LD_{50}) for white mice is only 0.33 and 0.20 mg kg^{-1}. Both compounds are several times more toxic than the widely known poisons such as hydrocyanic acid or strychnine. At the same time 1-arylsilatranes are almost harmless for cold-blooded animals (frogs, etc.), plants, and micro-organisms. Below the lethal dose (0.2–0.25 mg kg^{-1}), 1-phenylsilatrane is a powerful analeptic, i.e. it gives rise to motor excitation and intensifies the respiration of animals. It is interesting that for animals under narcosis 1-phenylsilatrane proves to be much less toxic. A dose ten times greater than the lethal dose causes only an excitation of respiration and convulsive movements of skeletal muscles. In animals with damaged central nervous systems 1-phenylsilatrane does not cause muscular convulsions even in doses of 1.5 mg kg^{-1} (introduced intravenously).

A wide variety of numerous experiments showed that 1-arylsilatranes do not affect the peripheral neuromuscular apparatus. The physiological activity of 1-arylsilatranes is due to their effect on a hitherto unknown enzyme system which is important for the function of the central nervous apparatus in warm blooded animals and which is absent or is less important for the activity of the central nervous system of cold blooded animals. For this reason, 1-arylsilatranes have no toxic effect on all living organisms at a lower level of evolutionary development.

The difference between 1-arylsilatranes and many of the familiar poisons is also indicated by the fact that enzymes such as cholinesterase and acetylcholinesterase are not inhibited by them.

The physiological activity and in particular the toxicity of silatranes vary within extremely wide limits, being determined mainly by the nature of the substituent R attached to the silicon atom itself (Table 4). The wide range of variation of this activity is indicated, for example, by the complete harmlessness of alkyl- and alkoxysilatranes (R = $CH_3C_2H_5O$ etc.).

Table 4. Toxicity of silatranes $RSi(OCH_2CH_2)_3N$ for white mice with intraperitoneal administration*.

R	LD_{50}, mg kg^{-1}	R	LD_{50}, mg kg^{-1}
p-$CH_3C_6H_4$	0.20	*p*-$CH_3C_6H_4O$	1270
C_6H_5	0.33	$C_6H_5CH_2$	1115
m-ClC_6H_4	4.4	CH_3O	2100
H	100	C_2H_5O	>5000
$CH_2(CH_2)_4CH$	150	CH_3	>5000
C_6H_5O	200	C_2H_5	>5000
p-$O_2NC_6H_4O$	700	$(CH_3)_2CH$	>5000
p-ClC_6H_4O	1050	$CH_2{=}CH$	>5000

*For 3,5-dimethyl-1-phenylsilatrane and 1-phenyl-2-carboxysilatrane, LD_{50} = 14.7 and 8.1 mg kg^{-1} respectively.

The introduction of methyl radicals into the silatrane system of 1-phenylsilatrane or the replacement of one of the oxygen atoms by a CH_2 group (1-phenyl-2-carbasilatrane) greatly reduces the toxicity of the compound. When the aromatic ring in 1-arylsilatranes is separated from the silatrane system by a methylene group (1-benzylsilatrane), the compound virtually loses its toxicity and the introduction of an oxygen atom into the Si–C_6H_5 bond (1-aryloxysilatranes) lowers the toxicity by several powers of ten. It is interesting that the hydrogenated analogue of 1-phenylsilatrane, i.e. 1-cyclohexylsilatrane, and also silatrane itself (1-hydrosilatrane) exhibit some, albeit low, toxicity.

In order to establish whether the structure of 1-arylsilatranes is specific for high physiological activity, we investigated the toxicity of open-chain silatrane analogues —a wide variety of 2-aminoethoxysilanes containing the Si–O–C–C–N group (derivatives of tri-, di-, and monoethanolamine) and also the initial amino-alcohols (Table 5). [295] It was found that all the organosilicon ethers of monoethanolamine in the series $R_{4-n}Si(OCH_2CH_2NH_2)_n$ with n = 1–3 are 2–9 times more toxic than $HOCH_2CH_2NH_2$ itself. At the same time the analogous derivatives of *NN*-dialkylaminoethanols usually prove less toxic than the corresponding amino-alcohol $HOCH_2CH_2NR_2$ (particularly for R = CH_3 or C_4H_9), or their toxicity is of the same order of magnitude (for R = C_2H_5).

Trialkylsilyl derivatives of triethanolamine are less toxic than triethanomaline itself, while the analogous diethanolamine derivatives are somewhat more toxic than diethanolamine itself. The toxicity of compounds in the

series $H_{3-n}N(CH_2CH_2OSiR_3)_n$, where R = CH_3 or C_2H_5 and n = 1–3, decreases appreciably as n increases. A change in the nature of the hydrocarbon substituent of the silicon atom in all types of the compounds investigated has little effect on the toxicity. On the whole, the toxicity,of organosilicon ethers of amino-alcohols is low and varies in the range from 120 mg kg^{-1} for $(C_2H_5)_2Si(OCH_2CH_2NH_2)_2$ to 4000 mg kg^{-1} for $N[CH_2CH_2OSi(C_2H_5)_3]_3$.

Table 5. Acute toxicity (LD_{50}) of 2-aminoethoxysilanes and 2-aminoethanols and dose which impairs the co-ordination of movement (ED_{50}) on intraperitoneal administration to white mice.

Compound	LD_{50}, mg kg^{-1}	ED_{50}, mg kg^{-1}
$HOCH_2CH_2NH_2$	1050	350
$(CH_3)_3SiOCH_2CH_2NH_2$	320	175
$(C_2H_5)_3SiOCH_2CH_2NH_2$	165	60
$(CH_3)_2Si(OCH_2CH_2NH_2)_2$	570	280
$(C_2H_5)_2Si(OCH_2CH_2NH_2)_2$	125	63
$CH_3Si(OCH_2CH_2NH_2)_3$	400	500
$C_2H_5Si(OCH_2CH_2NH_2)_3$	500	410
$C_6H_5Si(OCH_2CH_2NH_2)_3$	500	210
$HOCH_2CH_2N(CH_3)_2$	210	530
$(CH_3)_3SiOCH_2CH_2N(CH_3)_2$	620	265
$(C_2H_5)_3SiOCH_2CH_2N(CH_3)_2$	670	390
$HOCH_2CH_2N(C_2H_5)_2$	500	250
$(CH_3)_3SiOCH_2CH_2N(C_2H_5)_2$	630	50
$(C_2H_5)_3SiOCH_2CH_2N(C_2H_5)_2$	400	210
$(CH_3)_2Si[OCH_2CH_2N(C_2H_5)_2]_2$	720	64
$(C_2H_5)_2Si[OCH_2CH_2N(C_2H_5)_2]_2$	600	445
$CH_3Si[OCH_2CH_2N(C_2H_5)_2]_3$	600	385
$C_2H_5Si[OCH_2CH_2N(C_2H_5)_2]_3$	490	125
$C_6H_5Si[OCH_2CH_2N(C_2H_5)_2]_3$	560	—
$Si[OCH_2CH_2N(C_2H_5)_2]_4$	230	380
$HOCH_2CH_2N(C_4H_9)_2$	52	8
$(CH_3)_3SiOCH_2CH_2N(C_4H_9)_2$	640	600
$(C_2H_5)_3SiOCH_2CH_2N(C_4H_9)_2$	1650	2300
$(C_2H_5)_2Si[OCH_2CH_2N(C_4H_9)_2]_2$	2400	520
$(HOCH_2CH_2)_2NH$	1600	740
$[(CH_3)_3SiOCH_2CH_2]_2NH$	1250	380
$[(C_2H_5)_3SiOCH_2CH_2]_2NH$	1850	—
$(HOCH_2CH_2)_3N$	1450	110
$[(CH_3)_3SiOCH_2CH_2]_3N$	3500	1400
$[(C_2H_5)_3SiOCH_2CH_2]_3N$	4000	—
$(CH_3)_3SiOCH_2CH_2NC_5H_{10}$	400	—
$(C_2H_5)_3SiOCH_2CH_2NC_5H_{10}$	280	180
$(C_2H_5)_3SiOCH_2CH_2NHC_4H_9$	360	240
$(CH_3)_3SiOSi(CH_3)_3$	4500	

In the study of the effect of all the above aminoalkoxysilanes on the co-ordination of movement it was found that compounds of the type $(CH_3)_{4-n}Si[OCH_2CH_2N(C_2H_5)_2]_n$ with n = 1 and 2 are active at a dose smaller by a factor of 11–13 than the median lethal dose.

The data obtained convincingly demonstrate that the toxicity of 2-aminoethoxysilanes is scarcely due to the toxic effect of their hydrolysis products (one of these, hexamethyldisiloxane, for example, has LD_{50} = 4.5 g kg^{-1}) but is caused by the molecular structure as a whole. They also show that the high toxicity and physiological activity of 1-arylsilatranes cannot be attributed solely to the simultaneous presence in their molecule of the Si–aryl and Si–O–C–C–N bonds. Nor is it possible to explain the activity of 1-arylsilatranes by the presence in their molecules of the silatrane group $Si(OCH_2CH_2)_3N$, because 1-alkyl- and 1-alkoxy-silatranes are almost non-toxic. It might have been supposed that the physiological activity of 1-arylsilatranes is associated with the effect on the aromatic ring of the transannular co-ordinate bond Si ← N, which leads to an enhancement of its π-electron density and consequently its electron donor properties. However, the toxicity of 1-phenylgermatrane (smaller by a factor of 100 than that of 1-phenylsilatrane), which has a similar structure and dipole moment [358], suggests that the problem of the high physiological activity of 1-arylsilatrane still remains open, although it may be supposed that the much lower toxicity of 1-phenylgermatrane is due to its lower chemical stability.

The high physiological activity of 1-arylsilatranes suggested to us that other organosilicon compounds containing a nitrogen atom in the γ- or δ-position in relation to the silicon atom might be of definite interest in this respect. This was also indicated by a brief communication concerning the fairly high toxicity of compound (X):

$$(C_2H_5O)_2Si(CH_3)CH_2CH_2CH_2CH_2NH_2$$
(X)

(0.045 ml kg^{-1} when absorbed through the skin of the rabbit). [198,254]

Table 6. Acute toxicity (LD_{50}) of 3-aminopropylsilanes and dose which impairs the co-ordination of movements (ED_{50}) in white mice after intraperitoneal administration.

Compound	Formula	LD_{50}, mg kg^{-1}	ED_{50}, mg kg^{-1}
XI	$CH_3(C_2H_5O)_2Si(CH_2)_3\overline{N(CH_2)_4CH_2}$	6.6	8
XII	$CH_3(C_2H_5O)_2Si(CH_2)_3NH_2$	40	42
XIII	$CH_3(C_2H_5)_2Si(CH_2)_3NH_2$	47	—
XIV	$(C_2H_5)_3Si(CH_2)_3\overline{N(CH_2)_4CH_2}$	47	47
XIVa	$[(C_2H_5)_3Si(CH_2)_3\overline{NH(CH_2)_4CH_2}]Cl$	120	—
XV	$(C_3H_7)_3Si(CH_2)_3NH_2$	75	70
XVI	$CH_3(C_2H_5O)_2Si(CH_2)_3\overline{N(CH_2)_2OCH_2CH_2}$	86	40
XVII	$(C_2H_5)_3Si(CH_2)_3NH_2$	90	64
XVIII	$(CH_3)_3Si(CH_2)_3NH_2$	155	76
XIX	$C_2H_5(C_2H_5)_2Si(CH_2)_3NH_2$	120	100
XX	$(C_2H_5)_2C_6H_5Si(CH_2)_3NH_2$	140	62.5
XXI	$(C_2H_5)_2Si(CH_2)_3NHCH_2C_4H_3O$	185	280
XXII	$C_2H_5(C_2H_5O)_2Si(CH_2)_3NH_2$	215	130
XXIII	$(C_2H_5O)_3Si(CH_2)_3NH_2$	260	140
XXIV	$CH_3(C_2H_5O)_2Si(CH_2)_3\overline{N(CH_2)_3N(CH_2)CH_2CH_2}$	400	105
XXV	$CH_3(C_2H_5O)_2Si(CH_2)_3\overline{N(CH_2)_2SiCH_2CH_2}$	470	360
XXVI	$[(C_2H_5)_2SiCH{=}CHCH_2\overline{NH(CH_2)_4CH_2}]Cl$	110	31
XXVII	$[(C_2H_5)_2SiC{\equiv}CCH_2\overline{NH(CH_2)_4CH_2}]Cl$	195	80
XXVIII	$C_6H_4[Si(CH_3)_2CH_2CH_2CH_2NH_2]_2$-1,4	74	10
XXIX	$O[Si(CH_3)_2CH_2CH_2CH_2NH_2]_2$	80	60

To confirm this hypothesis, we investigated the toxicity and the effect on the co-ordination of movement of γ-aminopropyl substituted silanes and their unsaturated analogues. The data obtained (Table 6) show that, among compounds of this type, there are some fairly toxic [compound(XI) with LD_{50} = 6 mg kg^{-1}] and also compounds which fairly effectively reduce the motor activity and impair the co-ordination of movement [compounds (XXVI) and (XXVIII)] [294,298].

Among γ-aminopropylsilane derivatives, derivatives of bis-(3-aminopropylsilyl)benzene are of particular interest. For example, one of these [compound (XXVIII)] impairs the co-ordination of movement at a dose as low as 10 mg kg^{-1}, while at a dose of 4.8 mg kg^{-1} it reduces the body temperature by 3 deg.

It should be pointed out that the toxicity of the hydrochlorides of γ-aminopropylsilanes is reduced [compounds (XIV) and (XIVa)]. In the series of the hydrochlorides $[(C_2H_5)_3Si(CH_2)_nNH(CH_2)_4CH_2]Cl$ the toxicity decreases with increasing n. Thus for $n = 1$, 2, and 3, LD_{50} is respectively 60, 88, and 120 mg kg^{-1}.

We investigated the fungistatic and bacteriostatic activities of several dozen of nitrogen-containing organosilicon compounds of a wide variety of types [293,337]. Among these substances with a comparatively high activity were detected (Table 7).

Table 7. Minimum concentration (C) of nitrogen-containing organosilicon compounds suppressing the growth of micro-organisms.

Compound	Formula	Test microbe	C, mg ml^{-1}
XII	$CH_3(C_2H_5O)_2SiCH_2CH_2CH_2NH_2$	*Escherichia coli* 675	10.4
XV	$(n\text{-}C_3H_7)_3SiCH_2CH_2CH_2NH_2$	*Candida albicans* 67/846	41.7
		Epidermophyton Kaufmann Wolf 41	13.8
		Trichophyton gypseum 4/3	13.8
		Bac. mycoides 675	14.0
XXI	$(C_2H_5)_3SiCH_2CH_2CH_2NH$—	*Staphylococcus aureus haemolyticus* 209	10.4
		Bac. mycoides 675	10.4
XXX	$(CH_3)_2Si(CH_2Cl)CH_2CH(CH_3)CONH_2$	*Epidermophyton Kaufmann Wolf* 41	6.9
		Trichophyton gypseum 4/3	13.8

Although nitrogen-containing organosilicon compounds of a wide variety of structures have been investigated, only substances with the nitrogen atom in the γ-position in relation to the silicon atom proved to be active. Two of the compounds, listed in Table 7 [compounds (XV) and (XXX)], are only slightly inferior (by a factor of 1.8) in their fungistatic activity on *Trichophyton gypseum* to the fungicidal preparation nystatin widely used in clinical practice. Two other compounds effectively suppress gram-positive [compound (XXI)] and gram-negative [compound (XII)] bacteria.

There is no doubt that continued studies in this field will lead to the discovery of even more active organosilicon fungistatic and bacteriostatic substances which may find practical application, in particular for the formation of stable fungicidal and antibacterial coatings.

Thus we have shown that a wide variety of classes of nitrogen-containing organosilicon compounds containing both nitrogen and silicon atoms, separated from one another by three other atoms, exhibit useful and varied effects on the living organism. These are the most promising possible new silicon-containing medicinal preparations and pesticides. Nevertheless we discovered substances with a high physiological activity also among other classes of nitrogen-containing organosilicon compounds. For example, we found (together with D. P. Dremova) that compounds of the series $R_2NCH_2(CH_3)Si(OR')_2$ are insect repellents [335]. Some data on the activity of the compounds of this type are presented in Table 8.

We hope that further study of organosilicon insect repellents will make it possible to produce stable coatings with a similar property.

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The findings described above urgently necessitate development of a new branch of silicon chemistry—the chemistry, biochemistry, and pharmacology of biologically active organosilicon compounds, i.e. "bio-organosilicon chemistry". This should include a detailed study of the role of silicon in living organisms and the physiological processes and pathological and gerontological changes occurring in them, the search for compounds of this element with high and specific biological activity, and the study of the possible practical application of such compounds in medicine, veterinary practice, agriculture, and other branches of human activity.

Table 8. Repellent activity of $R_2NCH_2(CH_3)Si(OR')_2$ in relation to a culture of fleas *X. Cheopis* at a concentration of 20 g m^{-2}.

R	R'	Coefficient of repellent activity (after 24 h)
$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	73.9
$n\text{-}C_4H_9$	$iso\text{-}C_4H_9$	80.7
C_2H_5	$n\text{-}C_6H_{13}$	70.0
C_2H_5	$CH_2(CH_2)_4CH$	79.9
C_2H_5	$n\text{-}C_8H_{17}$	77.9

In this connection we cannot fail to quote the prophetic lines written as early as 1878 by the French genius Louis Pasteur: "There is a great future for the therapeutic applications of silicon".

It is to be hoped that the time is near when, as a result of the combined efforts of chemists, biochemists, pharmacologists, physicians, biologists, and agronomists, a multiplicity of new synthetic and natural physiologically active organic compounds of silicon, which will prove as useful to man as silicates and silicones, will begin to be produced industrially.

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Laboratory of the Chemistry of Organoelemental Compounds, Institute of Organic Synthesis of the Academy of Sciences of the Latvian SSR, Riga

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Degree of Branching in Polymeric Chains

V.A.Grechanovskii

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The degree of branching of polymeric chains is one of the most important molecular parameters which determine the physicomechanical and technological properties of the polymers.
The results of theoretical calculations of the influence of the degree of branching on the dimensions and nydrodynamic properties of the macromolecules are surveyed. The experimental results from the study of the properties and methods of synthesis of various model branched polymers are systematised. The problem of the molecular weight distribution of branched polymers and also experimental methods of determining the degree of branching of mono- and polydisperse polymers are considered briefly.

I. INTRODUCTION

The presence of branching in molecular chains leads to extensive changes in the physico-mechanical and technological properties of various polymers in comparison to the corresponding linear polymers. For example, branched divinylstyrene rubbers, polybutadienes, and other branched elastomers have less elasticity, lower breaking stress, etc.[1-4]; the decrease in the strength properties and the change in dynamical mechanical characteristics with increase in the degree of branching are characteristic also with such thermoplastic polymers as polystyrene, polyethylene, poly(vinyl chloride), etc.[5-7]. There are also significant differences in the rheological properties of linear and branched polymers. Thus at low loads (shear stresses) linear polymers and their melts flow like newtonian liquids and exhibit a viscosity lower than that of the branched polymers but under higher loads the flow departs from newtonian so that the viscosity of a branched polymer is less (or almost equal) to that of the linear[8,9]. Similar rules also hold for concentrated solutions. Hence like the regularity of the structure of the polymeric chains, the molecular weight, and the molecular weight distribution (MWD), the degree of branching is a most important molecular parameter of polymers.
Branching arises during polymerisation mainly as a result of reactions in which active centres are transferred to the polymer chain; during this either the loss (abstraction) of a hydrogen atom in one of the monomeric units or the interaction of active centres with double bonds of the polymer chain is possible. In radical polymerisation these reactions take place in the following way:

1. Loss of a proton, H:

$$\sim M_n^{\cdot} + P_m \rightarrow M_nH + P_{m(-H)}^{\cdot};$$

$$\sim M_n^{\cdot} + \sim CH_2{-}CHR{-}CH_2 \sim \rightarrow M_nH + \sim CH_2{-}\dot{C}R{-}CH_2\sim$$

2. Interaction with the double bond:

$$\sim M_n^{\cdot} + P_m \rightarrow \sim M_{n+m}^{\cdot};$$

$$\sim M_n^{\cdot} + \sim CH=CH\sim \rightarrow \sim \overset{M_n}{\overset{|}{\dot{C}H}}{-}CH\sim.$$

Here $\sim M_n^{\cdot}$ and P_m denote the "live" and "dead" polymeric links of degree of polymerisation n and m respectively. (Two "live" polymeric chains can take part in the interaction but usually this is less probable.) In the first instance so-called trifunctional branching nodes are formed, in the second, tetrafunctional nodes (the branches leave from two points separated by a C–C bond and the distance between them can be neglected).

Similar changes also take place in catalytic polymerisation by the formation of branched molecules of different functionality. Clearly, not one but several branching nodes can be formed in a single macromolecule (but usually with fixed functionality).

Branched polymers with f-functional nodes are also formed in widely employed syntheses for the common polycondensation of bi- and f-functional monomeric units and in the irradiation of polymers.

II. FUNDAMENTAL CONCEPTS

In dependence on length, long-chain and short-chain branches are distinguished. Branches of a length commensurate with that of the main chain are termed long-chain, and the present article will mainly consider long-chain branching. By the length of a branch we understand the distance between the two nearest nodes of the branching or the distance between the nearest pair of nodes of the branching the end of the chain. Examples are distinguished when all the branches have the same length

(branching with a fixed chain length) and when there is a random distribution of branch lengths. This shows that if the structure of a branched molecule is determined by the molecular weight of each branch then any structures with a specified total number of nodes and molecular weight for the macromolecule are equally probable. Depending upon the nature of the attachment of the branches, branched molecules can be divided into: (1) comblike (graft branching), where the branches are attached to a main chain (Fig. 1*a*) and (2) statistical, where the polymer does not have a main chain (Fig. 1*b*); such structures can arise because of secondary branching†.

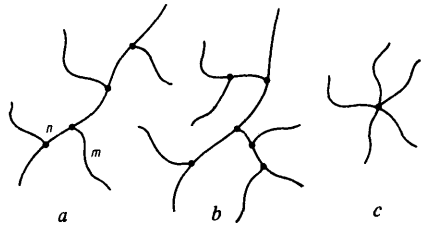


Figure 1. Models of branched macromolecules: *a*) comblike branched; *b*) statistically branched; *c*) starlike branched.

Whatever the nature of the branching the number of branches p is connected with the number of nodes b and the functionality of the branching by the relation:

$$p=(f-1)b+1. \quad (1)$$

A measure of the quantitative characteristic of branching is the branching density ρ, equal to the fraction of "cross-linked" (that is, having branching nodes) monomeric units in relation to their total number in the macromolecule:

$$\rho=\alpha\frac{b}{x} \quad (2)$$

where x is the degree of polymerisation, and α a constant depending on the functionality of the branching.

When during polymerisation the branching density exceeds some critical value ρ_c, which depends on molecular weight, an insoluble polymer starts to form, a gel which is a single space lattice [10,11]. Sometimes reference is made to the "degree of cross-linking" of polymeric molecules, characterised by the cross-linking (branching) parameter γ, where

$$\gamma=\rho/\rho_c \quad (3)$$

$\gamma = 1$ corresponds to the moment of gel formation.

III. UNPERTURBED DIMENSIONS OF BRANCHED MACROMOLECULES

In view of the small number of nodes in long-chain branching spectroscopic methods are used for identifying branched polymers. Therefore branching is investigated in dilute solutions, because the introduction of even one or two long-chain branching nodes leads to an appreciable decrease in the mean square dimensions of the macromolecules in comparison with linear ones of the same molecular weight.

The calculation of the undisturbed dimensions (that is, the dimensions in a θ-solvent) of branched macromolecules of various types has been carried out by various authors, who usually calculated the ratio of the mean square radii of inertia of branched $\overline{R}_b^2$ and linear $\overline{R}_l^2$ molecules of the same molecular weight; the g-factor is:

$$g=\overline{R}_b^2/\overline{R}_l^2. \quad (4)$$

For a small number of branching nodes this calculation can be made from purely geometric considerations. With a significant increase in the number of nodes statistical methods are employed. For example, for a branched macromolecule with one branching node a geometrical consideration gives [12]:

$$g=\sum_\lambda\left(\frac{3n_\lambda^2}{n^2}-\frac{2n_\lambda^3}{n^3}\right) \quad (5)$$

where n is the total number of segments (kinetically independent units) in the macromolecule), and n_λ the number of segments in the λ branch.

If a node has functionality f and the branch has a fixed length, that is, $n_\lambda = n/f$, then for such a star-shaped molecule we obtain from Eqn. (5):

$$g=\frac{3}{f}-\frac{2}{f^2} \quad (6)$$

in the particular example of trifunctional branching $g = 7/9$ and for tetrafunctional $g = 5/8$. For arbitrary branching the general equation for the g-factor has the form [13,14]:

$$g=\frac{6}{p(p+1)(p+2)}\left\{p^2+\sum_{\lambda,\mu}\nu_{\lambda\mu}\right\}. \quad (7)$$

Here $\nu_{\lambda\mu}$ is the number of branches between any two isolated branches λ and μ and the summation is over all the possible subdivisions of p branches of the macromolecule into different pairs (subsystems). Depending on the nature of the attachment of the branches and their distribution in lengths (at a given molecular weight and number of branching nodes) the sum will be somewhat different and the value of the g-factor will change correspondingly. From physical considerations it is evident that comblike branched macromolecules possess a large number of different subsystems compared with the statistically branched ones; fixing the branch lengths also leads to a decrease in the number of possible subsystems. Hence statistically branched macromolecules with a fixed branch length exhibit the least number of subsystems. The values of the g-factor should decrease in the same order. Accurate calculations have been made by Zimm and Stockmayer [12], Ptitsyn [15], and Kurata and Fukatsu [16].

In these studies values of the g-factor for various models of branching were calculated assuming that the branches are sufficiently long, that is, the distribution of the distances between the segments in the branches is a gaussian function. Table 1 gives the results of calculations [12,15,16] for various models of the branching. We note that the value of the g-factor for a given type of branching depends only on the number of branching nodes.

Tsvetkov developed an approximate method for calculating the dimensions of a branched chain in which the length of a side branch equals the length of the main chain; the

†Sometimes macromolecules in which f branches are attached to a single "point" (Fig. 1*c*) are regarded as a separate class of starlike macromolecules.

variation of the g-factor with the number of branches p for trifunctional nodes is of the form [17]:

$$g_3(p) = \frac{1}{p^2}\left\{25 + 6(p+3)\left[\frac{\ln(p+3)}{\ln 2} - 3\right]\right\} , \quad (8)$$

and that for the tetrafunctional is:

$$g_4(p) = \frac{1}{p^2}\left\{10 + 3(p+2)\left[\frac{2\ln(p+2)}{\ln 3} - 3\right]\right\}. \quad (9)$$

Table 1. Numerical values of the g-factor.

f	b	Statistically branched polymers		Comblike branched polymers		f	b	Statistically branched polymers		Comblike branched polymers	
		g_1	g_2	g_1	g_2			g_1	g_2	g_1	g_2
3	1	0.900	0.778	0.900	0.778	4	1	0.800	0.625	0.800	0.625
	2	0.829	0.712	0.829	0.712		2	0.691	0.545	0.691	0.545
	3	0.774	0.668	0.774	0.668		3	0.618	0.496	0.618	0.496
	4	0.730	0.633	0.733	0.638		4	0.566	0.460	0.569	0.465
	5	0.694	0.605	0.703	0.617		5	0.525	0.432	0.534	0.443
	6	0.663	0.581	0.679	0.601		6	0.493	0.410	0.508	0.428
	7	0.636	0.560	0.660	0.589		7	6.466	0.391	0.488	0.416
	8	0.613	0.542	0.645	0.580		8	0.443	0.374	0.472	0.407
	9	0.592	0.525	0.632	0.572		9	0.423	0.360	0.459	0.400
	10	0.573	0.510	0.622	0.566		10	0.406	0.347	0.448	0.394
	12	0.541	0.485	0.605	0.556		12	0.378	0.326	0.431	0.385
	15	0.505	0.454	0.587	0.546		15	0.344	0.301	0.414	0.375
	20	0.454	0.414	0.567	0.535		20	0.305	0.270	0.395	0.365
	25	0.418	0.384	0.555	0.529		25	0.277	0.248	0.384	0.359
						8	1	0.53	0.35	—	—
							2	0.41	0.28	—	—
							3	0.34	0.24	—	—

Note: g_1 random distribution of branch lengths; g_2 fixed branch lengths.

The results given in Table 1 relate to an idealised example in which monodisperse linear and branched polymers are compared and all the branched molecules have the same number of branching nodes. In practice, however, there is always a definite scatter both in the molecular weight and in the number of branching nodes for different macromolecules. Leaving aside the problem of the breadth of the molecular weight distribution, we will point out that for homogeneous polymers the molecules of which have a different number of branching nodes, Zimm and Stockmayer [12] obtained an equation relating the averaged mean square dimensions of molecules of such a polymer to the mean number of branching nodes b_n per molecule. For trifunctional branching nodes the mean value of the g-factor equals‡:

$$\langle g_3(b)\rangle = \left(\sqrt{1 + \frac{b_n}{7}} + \frac{4b_n}{9\pi}\right)^{-1/2} \quad (10)$$

and that for the tetrafunctional nodes is:

$$\langle g_4(b)\rangle = \left(\sqrt{1 + \frac{b_n}{6}} + \frac{4b_n}{3\pi}\right)^{1/2} . \quad (11)$$

The values of $< g(b) >$ are characteristic for fractions of the branched polymer if the fractionation proceeds only according to the molecular weights. These values are given in Table 1.

‡The sign $<>$ denotes the mean of the quantity considered.

It is noteworthy that not only do long-chain branchings lead to an appreciable decrease in the dimensions of the macromolecules; it is known that for comblike molecules with a large number of short side-chain attachments of the same length, the value of the g-factor is given by [18]:

$$g = \frac{n - \sum_\lambda n_\lambda}{n} = \frac{n_x}{n} \quad (12)$$

where n is the total number of segments in the macromolecule, n_λ the number of segments in the λ side chain, and n_X the number of segments in the "spine" of the macromolecule. Ptitsyn [15] obtained a similar relation:

$$g = \frac{m}{m+n} \quad (12a)$$

(see Fig. 1).

By short side branches is understood those branches with a length comparable with the distance between them ($m \simeq n$). Hence when there is a large number of short side attachments ($n_\lambda/n \ll 1$) the value of the g-factor can also differ considerably from unity. However, unlike the long-chain branching in this instance the dimensions of the macromolecules are determined mainly by the length of the spine; it is then possible in principle for 99% of the mass of the macromolecule to be centred in the side-chains of the branches. Such macromolecules can have anomalously small dimensions for a large molecular weight. As Eqns. (12) and (12a) show, the value of the g-factor depends not only on the number but also on the lengths of the side-chains, therefore the determination of the number of nodes solely from the g-factor cannot be considered reliable for short-chain branching.

Direct measurements of the mean sizes of the macromolecules can be made using a light scattering method but this method is as yet little used in analysing branching. The theory of the scattering of light by branched macromolecules has been developed only for certain particular instances [19-21], therefore these problems will not be discussed here. The present investigation of branching is now mainly on the basis of a study of the hydrodynamic behaviour of macromolecules in solutions (characteristic viscosity and sedimentation).

IV. HYDRODYNAMIC PROPERTIES OF BRANCHED MACROMOLECULES

Branched polymers in which the branching density does not exceed the critical value dissolve in the same solvents as do the linear polymers. However, in several studies it was noted that the solubility of branched polymers is less than that of linear, since the critical temperature of mixing of a polymer with a solvent for branched polymers is higher than for linear polymers of equal molecular weight [22,23].

In thermodynamically ideal solvents linear macromolecules can be regarded as unflowing coils with a gaussian distribution of the segments around the centre of gravity. The appearance of branching leads to a concentration of the segments and their more uniform distribution in the volume of the macromolecule, therefore the statistics of a branched macromolecule in solution are gaussian [25,26]. In this sense the effect of branching is opposite to the influence of phenomena of the volume effects (well studied theoretically) [10,24] in "good" solvents, where the "dilution" of the segments in the bulk of the macromolecule is observed.

1. Sedimentation and Diffusion of Branched Macromolecules

The sedimentation constant S and diffusion constant D of the macromolecules are connected with their dimensions by the coefficient of translational friction F_{tr} (here and subsequently reference is made to the sedimentation and diffusion constants extrapolated to infinite dilution):

$$S = \frac{M(1-\bar{v}\rho_0)}{NF_{tr}} \quad (13)$$

$$D = \frac{kT}{F_{tr}} \quad (14)$$

$$F_{tr} = P(\overline{R^2})^{1/2}\eta_0 = B\eta_0 \quad (15)$$

where M is the molecular weight, $\bar{v}$ the specific partial volume of the polymer, η_0 and ρ_0 are the viscosity and density of the solvent, N is Avogadro's number, k the Boltzman constant, and P the Flory constant, which characterises the hydrodynamic interaction of the macromolecules with the solvent in translational motion for linear polymers in a θ-solvent, $P = 5.11 \times \sqrt{6}$. The sedimentation and diffusion constants are determined by the first power of the hydrodynamically effective dimensions of B. Application of Eqns. (13)–(15) to linear and branched macromolecules gives:

$$\frac{S_b}{S_l} = \frac{D_b}{D_l} = \frac{P_l(\overline{R_l^2})^{1/2}}{P_b(\overline{R_b^2})^{1/2}} = \frac{P_l}{P_b}g^{-1/2}; \quad (16)$$

$$\frac{P_l(\overline{R_l^2})^{1/2}}{P_b(\overline{R_b^2})^{1/2}} = \frac{B_l}{B_b} = h; \quad (17)$$

$$\frac{S_b}{S_l} = \frac{D_b}{D_l} = \frac{F_{tr,b}}{F_{tr,l}}, \quad (18)$$

where h is the ratio of the dimensions hydrodynamically effective in forward motion; the subscripts b and l refer to branched and linear macromolecules.

On the basis of the Kirkwood and Riseman theory of the hydrodynamic properties of macromolecules [28,29], Stockmayer and Fixman [27], Ptitsyn [15], and Kurata and Fukatsu [16] made direct calculations of the ratio of the coefficients of friction and of the sedimentation and diffusion constants of branched and linear macromolecules of the same molecular weight. For starlike molecules with a fixed branch length the following relation was found [27] between the ratio of the hydrodynamic dimensions h and the branching functionality f:

$$h = \frac{f^{1/2}}{2 - f + \sqrt{2}(f-1)} \quad (19)$$

The values of h for comblike and statistically branched macromolecules were calculated by Ptitsyn [15] and by Kurata and Fukatsu [16]; the corresponding analytical expressions are extremely large and will not be given here; calculated values for the various types of branching are given in Table 2. It is noteworthy that concordant results were obtained in these studies [15,16].

Kurata and Fukatsu [16] showed that for statistically branched macromolecules the ratio P_b/P_l increases monotonically with increase in the branching density, tending to the asymptotic value of 1.34. As the branching density is increased, for graft branched macromolecules the value of the ratio P_b/P_l first rises then passes through a maximum and decreases, tending to 1.00 independent of the functionality of the branching. These results show that the hydrodynamically effective dimensions in translational motion of the macromolecules depend not only on the density but also the type of branching. In principle the relation $h = f(p)$ could be used for finding the branching type but in practice this is made difficult, since significant differences in the behaviour of the function $h = f(p)$ start only when the number of branching nodes reaches 30–40§.

Table 2. Numerical values of h.

f	b	Statistically branched polymers		Comblike branched polymers		f	b	Statistically branched polymers		Comblike branched polymers	
		h_1	h_2	h_1	h_2			h_1	h_2	h_1	h_2
3	1	0.972	0.947	0.972	0.947	4	1	0.938	0.892	0.938	0.892
	2	0.950	0.922	0.950	0.922		2	0.891	0.850	0.891	0.850
	3	0.931	0.903	0.931	0.903		3	0.864	0.820	0.864	0.820
	4	0.915	0.887	0.916	0.888		4	0.838	0.797	0.840	0.799
	5	0.901	0.873	0.903	0.876		5	0.817	0.778	0.820	0.782
	6	0.888	0.861	0.892	0.866		6	0.799	0.762	0.807	0.769
	7	0.878	0.850	0.883	0.858		7	0.782	0.748	0.791	0.757
	8	0.867	0.840	0.875	0.851		8	0.768	0.735	0.781	0.748
	9	0.855	0.831	0.868	0.845		9	0.755	0.724	0.771	0.740
	10	0.846	0.823	0.862	0.840		10	0.743	0.713	0.763	0.733
	12	0.830	0.807	0.852	0.830		12	0.723	0.695	0.749	0.721
	15	0.808	0.788	0.839	0.820		15	0.697	0.672	0.733	0.708
	20	0.779	0.760	0.825	0.807		20	0.664	0.642	0.714	0.692
	25	0.756	0.739	0.814	0.798		25	0.638	0.619	0.701	0.681
						8	1	0.81	0.72	—	—
							2	0.73	0.66	—	—
							3	0.68	0.62	—	—

Note: h_1 random distribution of branch lengths; h_2 fixed branch lengths.

2. Characteristic Viscosity of Branched Monodisperse Polymers

The characteristic viscosity, $[\eta]$, in a θ-solvent is connected with the unperturbed mean square dimensions of the test macromolecules by the following relation:

$$[\eta] = \Phi\frac{(\overline{R^2})^{3/2}}{M}; \quad (20)$$

where Φ is Flory's constant, characterising the hydrodynamic interaction of macromolecules with the solvent in rotational motion; for linear polymers in a θ-solvent $\Phi = 6^{3/2} \times 2.86 \times 10^{21}$. Evidently the characteristic viscosity depends not only on the dimensions of the macromolecules but also on the nature of their hydrodynamic interaction with the solvent. When allowance is made for this the characteristic viscosity is determined by the cube of the hydrodynamically effective dimensions A:

$$[\eta] = \frac{A^3}{M}. \quad (20a)$$

From Eqn. (20) the characteristic viscosity of the branched macromolecules should be less than that for linear polymers of the same molecular weight. The use of Eqns. (20) and (20a) for linear and branched polymers leads to the following relations:

$$\frac{[\eta]_b}{[\eta]_l} = \frac{\Phi_b}{\Phi_l}\left(\frac{\overline{R_b^2}}{\overline{R_l^2}}\right)^{3/2} = \frac{\Phi_b}{\Phi_l}\cdot g^{3/2}, \quad (21)$$

$$\frac{[\eta]_b}{[\eta]_l} = \frac{A_b^3}{A_l^3}. \quad (22)$$

§While this paper was in the press a paper by Berry [82] dealing with the calculation of the coefficient of translational friction of statistically branched macromolecules of comblike structure appeared.

The value of the ratio of the hydrodynamic interaction constants Φ_b/Φ_1 of branched and linear polymers is determined by the statistics of the macromolecular coil in the solution. Many calculations [15,16,27,30] have shown that the effect of branching on the geometric dimensions is more pronounced than on the hydrodynamic parameters, in other words, the hydrodynamic interaction of branched macromolecules with a solvent is stronger than that of linear, that is, $\Phi_b/\Phi_1 > 1$. Assuming that hydrodynamically effective dimensions in translational and rotational motion of macromolecules are the same, $A = B$, Stockmayer and Fixman [27] obtain for models of star-shaped branched molecules the following relation (in this instance the functionality agrees with the number of branches):

$$\frac{[\eta]_b}{[\eta]_1} = h^3 = \frac{f^{3/2}}{\{2 - f + \sqrt{2}(f-1)\}^{3/2}}. \quad (23)$$

On the other hand, for the model under consideration

$$g = \frac{3f-2}{f^2}. \quad (24)$$

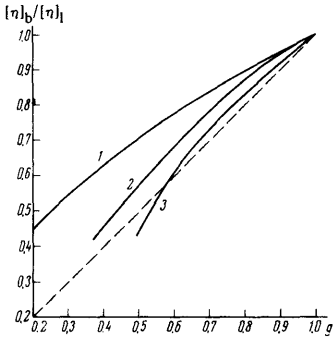


Figure 2. Variation of the characteristic viscosity with the g-factor: *1*) Zimm–Kilb theory; *2*) and *3*) calculated by Eqn. (25); *2*) Stockmayer and Fixman's results; *3*) Kurata and Fukatsu's results ($f = 3$, statistically branched); broken line, the relation $[\eta]_b/[\eta]_1 = g$.

On eliminating f from Eqns. (23) and (24), the variation of the ratio of the hydrodynamic dimensions, that is, the ratio of the characteristic viscosities (sedimentation constant) of branched and linear macromolecules with the g-factor can be found (Fig. 2, curve *1*). In practice, however, examples are seldom encountered in which the functionality of the branching exceeds 8. On also allowing for the fact that in this instance the presence of only one branching node is assumed it is evident that the use of Eqns. (23) and (24) is extremely limited in principle. Therefore Stockmayer and Fixman assume that the relation $h^3 = f(g)$ remains valid for any model of branching and propose to use it for finding not only the functionality but also the number of branching nodes if the relation $[\eta]_b/[\eta]_1$ is known.

Zimm and Kilb [30] attempted to find whether there is actually any general connection between the ratio of the characteristic viscosities of branched and linear macromolecules and the value of the g-factor beyond the dependence on the nature of the branching. On the basis of the Kirkwood–Riseman theory [28,29] of hydrodynamic properties of macromolecules, within the framework of the "pearl necklace" model, Zimm and Kilb directly calculated the value of the characteristic viscosity for two models of starlike branching of macromolecules: (1) one branching node with four branches of equal length; (2) one branching node with two long and eight short branches. The results of these calculations lead to the conclusion that for both branching models examined the following approximate relation is valid:

$$[\eta]_b/[\eta]_1 \cong g^{1/2}; \quad (25)$$

Zimm and Kilb also suggest that this equation can be applied with good approximation to any type of branched macromolecules.

It is noteworthy that the Stockmayer–Fixman and the Zimm–Kilb calculations were carried out for starlike macromolecules and *a priori* extension of results to comb-like macromolecules give rise to objections. We think that the more accurate relation $[\eta]_b/[\eta]_1 = f(g)$ for comb-like and statistically branched polymers can be obtained on the basis of calculations of hydrodynamically effective dimensions of macromolecules made by Kurata and Fukatsu [16] (Table 2). Here again it is suggested that the relation

$$[\eta]_b/[\eta]_1 = h^3 \quad (26)$$

is valid.

Fig. 2 gives the results of calculations of the relation $[\eta]_b/[\eta]_1 = f(g)$, which we made with allowance for Eqn. (26), according to Stockmayer and Fixman's and to Kurata and Fukatsu's results and according to Zimm and Kilb's theory. It should be noted that Eqn. (26) evidently over-rates the influence of branching on the value of the characteristic viscosity, especially in the range of high branching densities, where the hydrodynamic interaction increases considerably, therefore the true $[\eta]_b/[\eta]_1 = f(g)$ curves for models considered by Stockmayer and Fixman, and by Kurata and Fukatsu rule out some of the above references.

The existence of the relation $h = f(g)$ allows the degree of branching of a polymer with a narrow MWD to be evaluated on the basis of measurements of the characteristic viscosity or sedimentation (diffusion). Knowing the ratio of the hydrodynamic dimensions (that is, the ratio of the characteristic viscosities or sedimentation constants) of branched and linear macromolecules of equal molecular weight and of equal branching type, the corresponding ratio of geometric dimensions (the g-factor) and then from tables the number of nodes (branches) in a macromolecule can be found.

V. DEGREE OF BRANCHING IN POLYDISPERSE POLYMERS

Most of the synthetic polymers which are dealt with in practice are polydisperse. The degree of branching of polydisperse polymers is estimated by averaging the corresponding characteristics of monodisperse branched polymers. The concept of mean density of branching is introduced as a quantitative characteristic of branched polydisperse polymers. The number average branching density b_n is determined by the expression:

$$b_n = \frac{\sum_{x=1}^{\infty}\sum_{b=0}^{\infty} bP_{b,x}}{\sum_{x=1}^{\infty}\sum_{b=0}^{\infty} P_{b,x}}, \quad (27)$$

where $P_{b,x}$ is the number of molecules of degree of polymerisation x, having b branching nodes, and b_n the mean number of branching nodes for a single polymeric molecule. The weight average branching density b_w is determined similarly:

$$b_w = \frac{\sum_{x=1}^{\infty}\sum_{b=0}^{\infty} b_x P_{b,x}}{\sum_{x=1}^{\infty}\sum_{b=0}^{\infty} x P_{b,x}}. \quad (28)$$

Before analysing the value of the characteristic viscosity of polydisperse branched polymers we will examine the principal functions of MWD of branched polymers.

1. MWD of Branched Polymers

Branched polymers are usually characterised by wider molecular weight distribution functions than for linear ones, a polydispersity index determined as the ratio of the mean weight index of polymerisation x_w to the numerical mean x_n for branched polymers is usually greater than two, $x_w/x_n > 2$. Here we will consider some MWD functions typical for branched polymers.

The MWD of a polymer formed in the common statistical polycondensation of bi- and tetra-functional monomeric units is described by the distribution function given by Stockmayer [31], which can be represented as a system of equations:

$$P_{0,x} = x/y_n^2 \exp\{(x/y_n)(1+\gamma/2)\},$$
$$P_{b,x} = \frac{\gamma (x/y_n)^2}{2b(2b+1)(2b+2)} P_{b-1,x}, \quad (29)$$

where γ is the branching index—see Eqn. (3), y_n the number average degree of polymerisation of the corresponding linear polymer, which would be obtained were the tetrafunctional units replaced by the stoichiometric amount of bifunctional units, and a polymer with "most probable" MWD is formed. The mean degrees of polymerisation of the branched x and linear y polymers thus obtained are connected by the relations [31]:

$$x_w = \frac{y_w}{1-\gamma}; \quad (30)$$
$$x_n = \frac{y_n}{1-\gamma/4}; \quad (31)$$
$$y_w = 2y_n. \quad (32)$$

The branching parameter γ is connected with the number average b_n and the weight average b_w by the number of branching nodes by the following equations:

$$b_w = \frac{\gamma}{1-\gamma}; \quad (33)$$
$$b_n = \frac{\gamma}{4-\gamma}. \quad (34)$$

A variant of the Stockmayer function for polymers with trifunctional branching nodes (common polycondensation of bi- and tri-functional units) was obtained by Schultz [32]:

$$P_{0,x} = x/y_n^2 \exp\{-x/y_n(\gamma+1)\}; \quad P_{b,x} = \frac{\gamma (x/y_n)^2}{b(b+2)} P_{b-1,x}. \quad (35)$$

Fig. 3*a* shows a Stockmayer-type MWD for polymers with trifunctional and tetrafunctional branching nodes and various γ, the "most probable" distribution being given. Clearly the increase in the degree of branching leads to the appearance of high-molecular-weight "tails" and the MWD maximum is shifted to lower molecular weights; such regularities are actually observed in the synthesis of branched polystyrenes [33] and polybutadienes [34]. For a MWD describable by the system of equations (35), the following relations are obeyed:

$$x_w = \frac{y_w}{1-\gamma}; \quad (36)$$
$$x_n = \frac{y_n}{1-\gamma/3}; \quad (37)$$
$$b_w = \frac{2\gamma}{1-\gamma}; \quad (38)$$
$$b_n = \frac{{}^2/_3\gamma}{1-\gamma/3}. \quad (39)$$

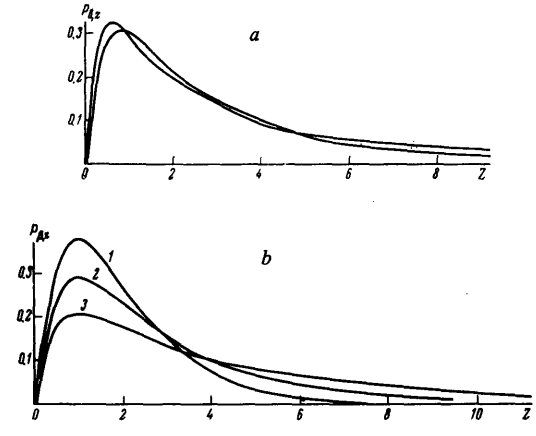


Figure 3. MWD of branched polymers, $Z = x/y_n$: *a*) MWD of the Stockmayer type, $f = 3:1$; *1*) $\gamma = 0.96$; *2*) $\gamma = 0.40$; *b*) MWD of the Beasley type, β: *1*) 0; *2*) 0.2; *3*) 0.499.

Another important distribution function was given by Beasley [35] for the MWD of polymers in the preparation of which the termination of the growing chains is brought about by disproportionation, conversion to the monomer, and conversion to a polymer (trifunctional branching), analytically the Beasley function is expressed by Eqn. (40) (Fig. 3*b*):

$$P_{\beta,x} = \frac{x/y_n^2}{(1+\beta x/y_n)^{1+1/\beta}} \quad (\beta < {}^1/_2), \quad (40)$$

where β is a long-chain branching parameter, equal to the ratio of the number of units in the side-branches and their total number in the macromolecule, with [35,36]:

$$x_n = \frac{y_n}{1-\beta}; \quad (41)$$
$$x_w = \frac{y_w}{1-2\beta}; \quad (42)$$
$$b_n = \frac{\beta}{1-\beta}; \quad (43)$$
$$b_w = \frac{1}{(1-\beta)(1-2\beta)} - 1. \quad (44)$$

Under comparable conditions the Beasley distribution is wider than the Stockmayer distribution. From Eqns. (30)–(34), (36)–(39), and (41)–(44) we obtain the frequently

used relations connecting the polydispersion of the polymer with the mean number of branching nodes:

$$\left.\begin{aligned}\frac{x_w}{x_n}&=\frac{2}{3}\frac{b_w}{b_n};\\ \frac{x_w}{x_n}&=\frac{2}{1-b_n};\end{aligned}\right\}\quad\begin{aligned}&\text{Stockmayer distribution}\\&\text{trifunctional nodes}\end{aligned}\qquad(45),\ (46)$$

$$\left.\begin{aligned}\frac{x_w}{x_n}&=\frac{1}{2}\frac{b_w}{b_n};\\ \frac{x_w}{x_n}&=\frac{2}{1-3b_n};\end{aligned}\right\}\quad\begin{aligned}&\text{Stockmayer distribution}\\&\text{(tetrafunctional nodes)}\end{aligned}\qquad(47),\ (47a)$$

$$\left.\begin{aligned}\frac{x_w}{x_n}&=\frac{1}{2}\left(\frac{b_w}{b_n}-1\right);\\ \frac{x_w}{x_n}&=\frac{2}{1-b_n}\end{aligned}\right\}\quad\text{Beasley distribution}\qquad(48),\ (48a)$$

Certain parameters of the branched polydisperse polymers with the Beasley-type and Stockmayer-type MWD are also shown in Table 3. Other MWD functions for branched polymers obtained in various polymerisation processes and also for the cross-linking and destruction were given detailed consideration by Bamford and Tompa [37], Katsura [38], Spiro [39], etc.

2. Characteristic Viscosity of Branched Polymers

We will assume that for monodisperse polymers the following relations are true:

$$[\eta]_b = g^{1/2}[\eta]_l, \qquad (49)$$

$$[\eta]_l = K_\eta x^a, \qquad (50)$$

where x is the degree of polymerisation, K_η and a are constants for the given series of polymer homologues.

Furthermore let $f(x)$ and $f(\gamma, x)$ be the weight functions of the distribution according to the degree of polymerisation for a linear and a diluted polymers, and γ a branching parameter determinable so that

$$f(\gamma, x)|_{\gamma\to 0} = f(x). \qquad (51)$$

On averaging in accordance with Eqns. (49) and (50) we obtain the following equation for the ratio of the characteristic viscosities of the branched and linear polydisperse polymers:

$$\langle[\eta]_b\rangle/\langle[\eta]_e\rangle = \frac{\int_0^\infty K_\eta g_x^{1/2} x^a f(x,\gamma)\,dx}{\int_0^\infty K_\eta x^a f(x)\,dx}. \qquad (52)$$

By using Eqns. (30) and (36) and taking into account that linear and branched polymers with the same mean weight are being compared, Eqn. (52) can be converted into [40]:

$$\langle[\eta]_b\rangle/[\eta]_e\rangle = (1-\gamma)^a \frac{\int_0^\infty g_x^{1/2} x^a f(\gamma, x)\,dx}{\int_0^\infty x^a f(x)\,dx}. \qquad (53)$$

The calculation of $<[\eta]_b>/<[\eta]_l>$ with the aid of Eqn. (53) is carried out as follows:

1. By using the MWD functions (29), (35), and (40), the number average values of the branching nodes b_n for various x are determined.

2. From the values for b_n, the corresponding values of $g_x^{1/2}$ are found on the basis of Stockmayer's equations (10) and (11).

3. By using the values found for x, $g_x^{1/2}$, and $f(\gamma, x)$ and replacing integration by summation the value of the numerator in Eqn. (53) is calculated.

4. The value of the denominator is expressed by elementary functions. A complete calculation of the ratio $<[\eta]_b>/<[\eta]_l>$ for polydisperse polymers with a Stockmayer-type MWD (with γ variable) was made on an electronic computer by Klib [40] for the tetrafunctional nodes and by Shultz [32] for trifunctional branching nodes (Table 3) and by Myers and Dagon [41] for a Beasley-type MWD.

Table 3. Ratio of the characteristic viscosities of branched and linear polymers of the same mean molecular weight (MWD of the Stockmayer type).

γ	$[\eta]_b/[\eta]_l$				
	$f=3$			$f=4$	
	$a=0.50$	$a=0.66$	$a=1.00$	$a=0.50$	$a=0.68$
0.1	0.975	0.974	0.978	—	—
0.2	0.948	0.946	0.954	0.94	0.94
0.3	0.917	0.914	0.926	—	—
0.4	0.880	0.875	0.892	0.87	0.87
0.5	0.839	0.832	0.855	—	—
0.6	0.787	0.778	0.807	0.77	0.76
0.7	0.722	0.709	0.744	—	—
0.8	0.633	0.614	0.654	0.61	0.58
0.9	0.490	0.462	0.501	0.47	0.43
0.92	0.450	0.421	0.463	—	—
0.94	0.402	0.371	0.415	—	—
0.96	0.342	0.308	0.364	—	—

The results of Table 3 can be used in evaluating the branching of polydisperse polymers on the basis of measurements of characteristic viscosity. For this a knowledge of the characteristic viscosity of the linear polymer with the "most probable" distribution and the same weight mean molecular weight is necessary. If the value of x_w is known the corresponding value of $<[\eta]_l>$ can be determined by using the equation for the dependence of characteristic viscosity on molecular weight for linear monodisperse polymers

$$[\eta]_l = K_\eta x^a, \qquad (50a)$$

which are usually found in investigating hydrodynamic characteristics; the corresponding equation for the weight mean degree of polymerisation in a θ-solvent has the form [42]:

$$\langle[\eta]_l\rangle = \frac{K_\eta}{1.14} x_w^a. \qquad (54)$$

In principle the ratio $<[\eta]_b>/<[\eta]_l>$ can be compared at the same values of number mean molecular weight, but this method appears less sensitive to branching than that described above [40].

It is noteworthy that estimation of branching of polydisperse polymers with the aid of the $<[\eta]_b>/<[\eta]_l>$ dependence, strictly speaking, is valid only in those instances when the branching reaction leads to the departure of the MWD of polymers from the most probable.

The influence of the form of the MWD functions on the value of $<[\eta]_b>/<[\eta]_l>$ is clear from Table 4, which gives values calculated on the basis of Beasley-type [41] and Stockmayer-type [32] MWD (trifunctional nodes) at equal values

of x_w/x_n (the MWD of a linear specimen is considered "most probable"), with

$$\gamma = \frac{3\beta}{2-\beta}. \quad (55)$$

At equal values of x_w/x_n the Beasley distribution is wider than the Stockmayer distribution; as Table 4 shows, this leads to some decrease (by 6–14%) in the values of $\langle[\eta]_b\rangle/\langle[\eta]_l\rangle$. The Beasley distribution is known to somewhat overestimate the breadth of the experimentally observable curves[41,42] of branched polymers, therefore the use of results obtained with the aid of the Stockmayer equation is evidently more correct.

Table 4. Ratio of the characteristic viscosities of branched and linear polymers depending on the MWD of the branched polymer ($f = 3$).

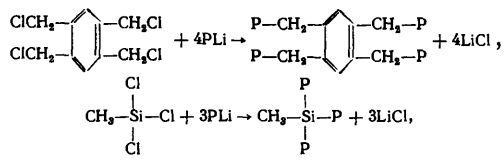
β	x_w/x_n	γ	$\langle[\eta]_b\rangle/\langle[\eta]_l\rangle$	
			Beasley distribution	Stockmayer distribution
0.05	2.11	0.077	0.922	0.981
0.10	2.25	0.158	0.901	0.960
0.15	2.43	0.243	0.876	0.935
0.20	2.67	0.333	0.847	0.906
0.25	3.00	0.429	0.809	0.869
0.30	3.50	0.529	0.763	0.826
0.35	4.33	0.636	0.700	0.766
0.40	6.00	0.750	0.612	0.680
0.45	11.0	0.871	0.465	0.542

In concluding this section it must be emphasised that all the calculated values of $\langle[\eta]_b\rangle/\langle[\eta]_l\rangle$ obtained under the condition that Eqn. (49) is valid are derived, strictly speaking, for the polymer solvent θ-system ($\alpha = 0.5$), therefore the problem of measurements in "good" solvents for the purpose of evaluating the branching still remains open, and corresponding experimental results will be considered below.

VI. SYNTHESIS AND INVESTIGATION OF MODEL BRANCHED POLYMERS

In most polymerisation processes it was previously impossible to predict the number of nodes associated with a single polymeric molecule, the lengths of the branches, the nature of their distribution, or even the functionality of the branching. Therefore it is very difficult to make a strict comparison between the values calculated theoretically under definite conditions and the same quantities observable experimentally. With the aim of surmounting this difficulty attempts were made to synthesise model branched polymers with a geometry known beforehand.

Starlike macromolecules can serve as the simplest models. This type of model polymer is synthesised with the aid of "living" polymeric chains and bonding agents such as 1,2,4,5-tetrachlorobenzene, silicon tetrachloride, methyltrichlorosilane, etc. Several papers[44–48] describe methods of production and give structural characteristics for tri- and tetra-functional starlike polymers of styrene and butadiene; the synthesis proceeds as follows:



where PLi denotes a "live" polymeric chain.

Ideally all the chlorine atoms are replaced by a polymer anion; hence if the initial polymer molecules have a narrow MWD, as a result almost monodisperse branched polymers with a tripled or quadrupled molecular weight are formed. In practice, as a result of incomplete replacement and of side-reactions a mixture of molecules of different molecular weight and functionality is obtained, however, the choice of appropriate conditions gives an overwhelming yield of molecules of the specified structure.

Table 5. Characteristic of branched polystyrenes[45,46,48].

No.	$10^{-3}M_w$	p	M_w/M_n	$[\eta]$ good solvent	$[\eta]_\theta$	$[\eta]_b/[\eta]_l$ good solvent	$[\eta]_b/[\eta]_l$ θ-solvent	$[\eta]_b/[\eta]_l$ theory
				$f=3$	$b=1$			
1	170	3.0	—	0.563	0.288	0.90	0.94	
2	258	2.8	—	—	0.360	—	0.84	0.88*
3	348	2.6 3.1	0.99	0.976	0.435	0.88	0.85	0.85**
				$f=4$,	$b=1$			
1	11	3.9	—	—	0.077	—	0.86	
2	215	3.7	—	—	0.309	—	0.79	
3	363	3.9 3.9	—	—	0.390	—	0.75	0.79*
4	257	4.9 4.1	—	0.705	0.309	0.84	0.82	0.71**

*Zimm–Kilb theory.
**Stockmayer–Fixman theory.

Furthermore, to obtain polymers with high homogeneity both in respect of molecular weights and of the functionality of branching further fractionation is employed, which in this instance is especially effective owing to the great difference in the molecular weights. Sufficiently homogeneous, but low-molecular-weight, branched polymers are evidently formed in the synthesis of polyamides of star structure[49], and also of polyhedra from monodisperse blocks of polyethylene glycols with the aid of the trichloride of trimesic acid and other compounds[50]. Some experimental results for model branched (starlike structure) polymers of styrene are given in Table 5, where p is the value found experimentally for the mean number of branches attached to one molecule.

A method of controlled synthesis making use of the chain transfer reaction to a polymer (with narrow MWD) introduced earlier into the reaction zone has been used[51] for obtaining comblike trifunctional poly(vinyl acetates) with a fixed side-chain length, and with random distribution of the branches along the main "spine". Homogeneous branched polymers with short side-chains of known number and length were thus obtained; statistically branched poly(vinyl acetates) have been synthesised[52]. Fig. 4 and Table 6 give some results from published studies[52,53].

From Tables 5 and 6 and Fig. 4 and also from other experimental results[30,49,50], the appearance of branching actually leads to a decrease in the characteristic viscosity of the corresponding polymers in comparison with the linear ones of equal molecular weight, and the viscosity of the statistically branched polymers is less than that of the comblike ones. The variation predicted theoretically for a θ-solvent of the ratio of the characteristic viscosities of branched and linear polymers at a fixed molecular weight[30], see Eqn. (25), is obeyed satisfactorily for star-like polymers of various chemical structures.

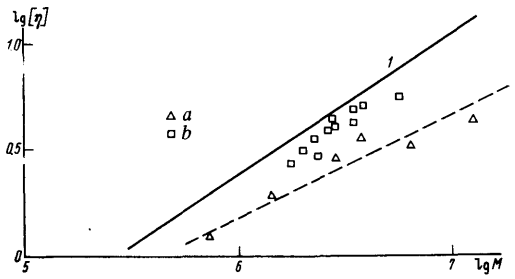


Figure 4. Variation of the characteristic viscosity of poly(vinyl acetates) in benzene at 35°C: *1*) linear structure, $[\eta] \simeq M^{0}$;[68] *a*) statistical branching, $[\eta] \simeq M^{0.47}$; *b*) comblike branching.

It is noticeable, however, that most of the model polymers contained only one branching node, therefore it is evidently still early to extend rule (25) to the region of high branching densities. Furthermore in some instances, for example, for polyethylenes[43] of the high pressure type, poly(vinyl acetates)[53], and other polymers, appreciable departures from the rule are observed, namely, the number of nodes calculated with the aid of Eqn. (25) is greater than expected and for these polymers the relation

$$[\eta]_b/[\eta]_l = g^{\epsilon}, \qquad (56)$$

where $\epsilon > \frac{1}{2}$, holds, that is, Eqn. (25) underestimates the effect of branching.

From Table 6 it is evident that the value of $g^{1/2}$ systematically exceeds the ratio $[\eta]_b/[\eta]_l$ even in a good solvent; from this it follows that when there are a large number of short-chain branches Eqn. (25) also underestimates the effect of branching on the hydrodynamic properties.

Such anomalies are not remarkable, they must be expected at high branching densities, owing to the change in Φ_p (by analogy with P_p). Results on the model branched polymers with a considerable number of branching nodes are still extremely few and relate to polymers with short side-chains[51,53,54].

From the example of poly(vinyl acetate) (Table 6) clearly the ratio $[\eta]_b/[\eta]_l$ in a good solvent is usually greater than that in a θ-solvent and the value of the g-factor characterising the ratio of the dimensions in a θ-solvent is less than the directly measured ratio of the dimensions. This regularity agrees with a stated[55,56] viewpoint that volume effects should be stronger for branched polymers than for linear ones, therefore the characteristic viscosity of branched polymers should increase with improvement in the quality of the solvent more rapidly than the viscosity of the linear ones. However, on assuming that the Flory swelling coefficients α of linear and branched macromolecules are connected by the relation[53]:

$$\frac{\alpha_b^5 - \alpha_b^3}{\alpha_l^5 - \alpha_l^3} = \frac{C_b}{C_l} g^{-1/2}, \qquad (57)$$

where C_b and C_l are constants, which depend on statistics of branched and linear macromolecular coils in the solution, then the difference in the values of the ratios $([\eta_b]/[\eta]_l)_0$ and $([\eta]_b/[\eta]_l)$, should become appreciable only when the molecular weight becomes sufficiently high (~ 500 000). This can explain the fact that this regularity, observable for very high-molecular-weight polymers of vinyl acetate, was not observed for different model structures (Table 5) and the statistically branched polymers of lesser molecular weight[22,36,57,58].

Table 6. Characteristics of branched poly(vinyl acetates)[51-53].

No.	$10^{-6}M_w$	Molec. wt. of 1 branch	b	Wt. fraction of polymer in branches	g	$g^{1/2}$	$[\eta]_b/[\eta]_l$ good solvent	$[\eta]_b/[\eta]_l$ θ-solvent	R_b^2/R_l^2 good solvent
	12.6	—	—	—	0.32	0.57	0.35	—	0.58
	6.43	—	—	—	0.36	0.60	0.40	—	0.65
3	3.76	—	—	—	0.54	0.74	0.62	—	0.68
4	2.80	—	—	—	0.50	0.71	0.59	—	0.68
5	1.43	—	—	—	0.55	0.74	0.63	—	0.87
6	0.73	—	—	—	0.62	0.79	0.71	—	0.89
7	3.81	59	26	0.38	0.62	0.79	0.84	—	—
8	2.80	59	9	0.18	0.82	0.91	0.82	—	0.97
9	2.33	40	26	0.44	0.56	0.75	0.66	—	—
10	1.68	40	10	0.24	0.77	0.88	0.77	—	—
11	2.00	18.5	27	0.25	0.75	0.87	0.79	—	0.95
12	2.24	18	41	0.33	0.67	0.82	0.91	—	0.99
13	2.09	18	33	0.29	0.72	0.85	0.80	—	0.89
14	2.71	24	29	0.26	0.74	0.89	0.90	—	1.01
15	3.67	24.4	67	0.48	0.52	0.73	0.74	—	0.90
16	3.21	24.4	45	0.36	0.64	0.80	0.74	—	0.82
17	5.60	106	17	0.33	0.67	0.84	0.70	0.51	0.92
18	2.65	74.8	7	0.20	0.78	0.90	0.80	0.75	0.97
19	3.43	67	19	0.37	0.63	0.79	0.74	0.73	0.85
20	3.29	61	17	0.31	0.69	0.84	0.75	0.50	0.90
21	4.11	63.5	29	0.45	0.55	0.76	0.67	—	0.83
22	3.45	47	19	0.26	0.74	0.86	0.85	—	0.90
23	3.96	43.7	33	0.37	0.64	0.80	0.67	—	0.90

The synthesis of model branched polydisperse polymers with the aim of verifying the corresponding theoretical relations is a much more complex task. Nevertheless, attempts were made to synthesise polymers of vinyl acetate with a known degree of branching (that is, with b_n and b_w) and known MWD, using the method of controllable polymerisation with transfer of chains to the polymer. It has been found[36] that the value of the ratio $\langle[\eta]_b\rangle/\langle[\eta]_l\rangle$ is almost independent of the quality of the solvent, as for monodisperse polymers. Furthermore it has been shown that for the vinyl acetate polymers investigated the relation between the value of $\langle[\eta]_b\rangle/\langle[\eta]_l\rangle$ and the weight mean number of branches b_w there is just the same correlation as between $\langle g^{1/2}\rangle$ and b_w for polymers with a Stockmayer distribution[31]:

$$\langle g^{1/2}\rangle = \left(\frac{6}{b_w}\right)^{1/2}\left\{\frac{1}{2}\frac{2+b_w^{1/2}}{b_w}\ln\frac{(2+b_w)^{1/2}+b_w^{1/2}}{(2+b_w)^{1/2}-b_w^{1/2}} - 1\right\}^{1/2}. \qquad (58)$$

From this there must be a relation of type (25) in this instance:

$$\frac{\langle[\eta]_b\rangle}{\langle[\eta]_l\rangle} = \langle g^{1/2}\rangle. \quad (25a)$$

However, it was shown that this agreement can be accidental and can vary with the nature of the reactions which lead to the branching of the polymeric chains.

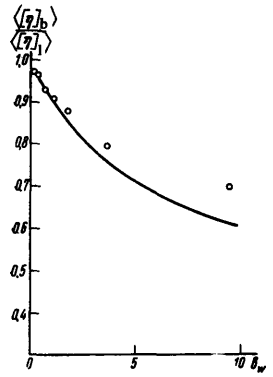


Figure 5. Variation of $[\eta]_b/[\eta]_l$ with the branching density for polymers with a Stockmayer-type MWD, with experimental points plotted from published results [36].

The decrease in the ratio $\langle[\eta]_b\rangle/\langle[\eta]_l\rangle$, expressed directly as a function of the number of branching nodes b_w, does not agree quite so well with the corresponding calculated relation obtained for trifunctional branched polymers with a Stockmayer-type MWD—calculated from the results of Table 4 and Eqn. (38), —see Fig. 5.

VII. VARIATION OF THE HYDRODYNAMIC PARAMETERS OF BRANCHED POLYMERS WITH MOLECULAR WEIGHT

The relations

$$[\eta]_l = K_{\eta l} M^{0.5}, \quad (59)$$

$$S_l = K_{Sl} M^{0.5}, \quad (60)$$

where $K_{\eta l}$ and K_{Sl} are coefficients which remain constant for a given series of polymer homologues, hold for linear monodisperse polymers in a solvent. In good solvents the value of the exponent in Eqns. (59) and (60) differs from 0.5. Most experimental studies on the investigation of branching have been carried out in good solvents and the dependence of the characteristic viscosity of branched polymers on molecular weight in logarithmic coordinates is usually bent towards the abscissa axis [22,33,59-62]. The explanation for this is that with increase in the molecular weight there is usually an increase in the branching density, therefore the dependence of the characteristic viscosity on molecular weight will be weakened, and the corresponding dependence of the sedimentation constant will be intensified; Eqns. (59) and (60) will become:

$$[\eta]_b = K_{\eta b} M^{0.5-\delta}, \quad (61)$$

$$S_b = K_{Sb} M^{0.5+\varphi}. \quad (62)$$

We will first examine the change in characteristic viscosity; from (59) and (61) we obtain:

$$[\eta]_b/[\eta]_l = K_1 M^{-\delta}. \quad (63)$$

In practice the greatest interest is in statistical and comblike branched macromolecules; it will be assumed that the increase in their molecular weight takes place by successive addition of branches of equal length with retention of the functionality of the branching. On assuming the correctness of the relation:

$$\langle[\eta]_b\rangle/\langle[\eta]_l\rangle = h^3,$$

we have:

$$h^3 = K' M^{-\delta}. \quad (64)$$

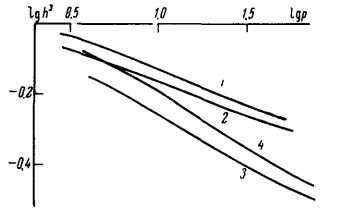


Figure 6. Variation of the ratio of the hydrodynamic dimensions of comblike branched and linear macromolecules with the number of branches: *1*) random distribution of branches with lengths $f = 3$; *2*) branches of equal length, $f = 3$; *3*) branches of equal length, $f = 4$; *4*) random distribution of branch lengths, $f = 4$.

Fig. 6 shows the relation:

$$\lg h^3 = f(\lg M)$$

for comblike branched macromolecules, $f = 3$ or 4, at a fixed branch length, calculated from Kurata and Fukatsu's results, where the number of branches is taken as a measure of the molecular weight; Fig. 6 also gives curves for the random distribution of the branches in length. Treatment of the results in Fig. 6 leads to the following results:

$f = 3$ { $\delta = 0.19$ branches of fixed length, $\delta = 0.20$ random distribution of branch lengths;

$f = 4$ { $\delta = 0.29$ branches of fixed length, $\delta = 0.31$ random distribution of branch lengths.

The values of δ are approximate (they were calculated by neglecting the low curvature of the curves discussed) and correct when the branching nodes lie between 3 and 20.

Earlier [58] for polymers with 1–4 trifunctional branching nodes and fixed branch lengths the value $\delta = 0.09$ was obtained by the relation

$$[\eta]_b/[\eta]_l = g^{1/2}$$

and $\delta = 0.12$ by calculation from Kurata and Fukatsu's results for the initial form of $h^3 = f(g)$ (1–4 nodes). Experimental results for dextranes [64] poly(vinyl acetates) [53], and polysiloxanes [65,66] with a large number of trifunctional

branching nodes, and for polybutadienes with a small number of nodes [47,63] agree satisfactorily with these calculations; for poly(vinyl acetates) $\delta = 20$, for polybutadienes $\delta = 0.09$, and for polysiloxanes $\delta = 0.22$ and 0.30.

Examples where the increase in molecular weight occurs only as a result of an increase in the functionality of the branches (a tenfold change in molecular weight produces a change in functionality from 3 to 30) will not be considered here because of their low practical importance. The value of δ differs from zero only if the increase in molecular weight is accompanied by an increase in the number of branching nodes because of their functionality; when the increase in molecular weight is due solely to the lengthening of the branches at $f = \text{const}$, $p = \text{const}$, then $\delta = 0$. Since

$$S_b / S_l = h^{-1},$$

it is evident that $\varphi = \delta/3$. Hence whereas the absolute value of the ratio of characteristic viscosities or sedimentation constants of the branched and linear macromolecules determine the length of the side-chains their dependence on molecular weight (especially in the range $b > 3$) can serve as an indicator of the functionality.

VIII. TREATMENT OF THE EXPERIMENTAL DATA IN STUDYING BRANCHING

As what has been said above shows, for a definite degree of branching of any polymer its hydrodynamic parameters must be compared with the parameters of the corresponding linear polymer of equal molecular weight, in other words, it is necessary to know the constants in the relation

$$[\eta]_l = K_l M^a \qquad (65)$$

for the linear polymer. However, this relation is not always known previously, and sometimes even the synthesis of the linear polymers presents difficulties. There are two main methods of studying branching in those instances when relation (65) is unknown. In both instances preliminary separation of the test polymer into a series of homogeneous fractions is necessary. The first method, based on the determination of the molecular weights of the fractions and working in a θ-solvent, was first used in studying branching in polymers of butadiene and isoprene [22,59,63].

Extension of the Flory theory of polymer solutions to branched molecules leads to the following relation [59]:

$$[\eta]^{2/3}/M^{1/3} = K_l^{2/3} g_{[\eta]} + 2C_M \psi K_l \frac{M}{[\eta]} g_{[\eta]}^{1/2}\left(1 - \frac{\theta}{t}\right); \qquad (66)$$

where ψ and C_M are constants for a given polymer–solvent system and

$$g_{[\eta]} = ([\eta]_b / [\eta]_l)^{2/3}.$$

From this equation, clearly whereas for linear polymers the relation at the temperature $T = \theta$ (in a θ-solvent) is expressed by a straight line parallel to the abscissa axis, for branched macromolecules this relation should have the form of a curve with negative slope, since $g_{[\eta]}$ in a disordered distribution of branching nodes decreases with rise in molecular weight. However, since as $M \to 0$ the number of branching nodes in the macromolecule also tends to zero and consequently $g \to 0$, the limiting value of $[\eta]^{2/3}/M^{1/3}$ remains as before equal to $K_l^{2/3}$. Hence by constructing this relation for branched polymers it is possible to determine the value of K_l and then by using the ratio $[\eta]_b/[\eta]_l$ to find the number of branches in the macromolecules of any molecular weight. Typical examples of the relation

$$[\eta]^{2/3}/M^{1/3} = f(M/[\eta])$$

for K-polybutadiene polymers obtained at various temperatures [22] are given in Fig. 7.

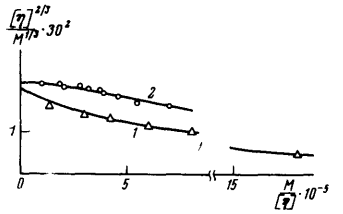


Figure 7. Variation of $[\eta]^{2/3}/M^{1/3}$ with $M/[\eta]$ in a solvent for polybutadienes of various structures: *1*) strongly branched; *2*) weakly branched.

Branching affects the hydrodynamic properties and dimensions, therefore there is a possibility in principle of obtaining information about the branching of macromolecules by direct measurement of any pair of hydrodynamic parameters connected with the coefficients of translational (diffusion, sedimentation) and rotational (characteristic viscosity) friction. This was first discussed by Tsvetkov [67].

This method of evaluating branching, based on combined measurements of sedimentation and characteristic viscosity, was proposed by Blachford and Robertson [68]; it is not necessary to know the molecular weight. It is known that

$$[\eta]_l = K_l M^a; \qquad (67)$$

$$S_l = K_s M^{\frac{1-a}{3}}. \qquad (68)$$

From Eqns. (67) and (68) we obtain

$$S_l = A[\eta]_l^{\gamma}; \qquad (69)$$

where A is a constant and

$$\gamma = \frac{2-a}{3a}. \qquad (70)$$

Applying the Flory theory to linear and branched polymers and assuming that

$$\Phi_l^{2/3} P_l^{-1} \cong \Phi_b^{2/3} P_b^{-1}, \qquad (71)$$

Blachford and Robertson [68] obtain

$$S_l [\eta]_l^{1/3} = S_b [\eta]_b^{1/3}. \qquad (72)$$

On substituting Eqn. (69) in (72) we have

$$A[\eta]_l^{\frac{3\gamma+1}{3}} = S_b [\eta]_b^{1/3}. \qquad (73)$$

Eqn. (73) is the principal one in this method; if γ, A, S_b, and $[\eta]_b$ are known, then the quantity $[\eta]_l$ can be obtained from Eqn. (73) and then the number of nodes in the macromolecules can be found in the usual way through the g-factor. A and γ are determined from the graph of $\lg S$ against $\lg[\eta]$ for fractions of the polymer being investigated, part of which is usually linear. An example of

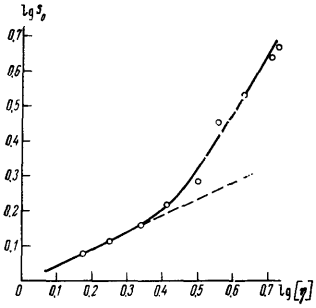


Figure 8. Variation of the sedimentation constants with the characteristic viscosity in benzene for fractions of butadienestyrene copolymer. The broken line corresponds with polymers of linear structure.

such a relation for fractions of emulsion butadienestyrene rubber are given in Fig. 8, and from the initial slope of the graph $A = 0.944$ and $\gamma = 0.61$. This method was used also for studying branching in polyurethanes [69]. The use of θ-solvents increases the accuracy of the method and its resolving power.

IX. OTHER METHODS OF DETERMINING DEGREE OF BRANCHING

The second virial coefficient A_2 is a measure of the interaction of polymer segments with one another in dilute solutions. The value of A_2 depends on the form of the intersegmental interaction potential and the statistics of the macromolecular coil in solution, approximate calculations of A_2 for certain models of starlike branched macromolecules have been given [70,71]. However, at present there is no complete and rigorous theory connecting the value of the second virial coefficient with the structure of branched macromolecules. The virial coefficient can be determined from osmometric and light scattering measurements¶:

$$\pi/c = \frac{RT}{M_n}(1 + A_2c + \ldots), \tag{74}$$

$$Kc/R_0 = \frac{1}{M_w}(1 + 2A_2c + \ldots), \tag{75}$$

where π is the osmotic pressure, R_0 the relative intensity of scattered light, c the concentration, and K a constant.

Extension of the theory of solutions of linear polymers to branched ones leads to the following approximate equation [44]:

$$(A_2)_b/(A_2)_l \cong g^{1/2}\left(\frac{\alpha_b}{\alpha_l}\right)^3, \tag{76}$$

where α_b and α_l are the swelling coefficients of linear and branched macromolecules respectively. Eqn. (76) is further simplified in the limiting case of large volume effects (high-molecular-weight polymer in a good solvent) [53]:

$$(A_2)_b/(A_2)_l = g^{1/2}. \tag{77}$$

¶Calculations of the value of the second virial coefficient for comblike branched polymers of various structures have recently appeared [80,81].

This result, allowing for Zimm–Klib calculations, agrees with the results of Krigbaum and Trementozzi [56], who suggested that for polymers of equal molecular weight the relation

$$(A_2)_b/(A_2)_l \cong \frac{[\eta]_b}{[\eta]_l} \tag{78}$$

is valid.

The experimental results [44,56] show that this relation is well confirmed for polymers with a narrow MWD. Hence the second virial coefficient is also somewhat sensitive to branching, like the value of the characteristic viscosity, but a more reliable theoretical basis and accuracy of measurements makes a study of the hydrodynamic parameters preferable.

A qualitative index of the presence of long-chain branching is the increased value of the Huggins constant K' in the equation for the concentration dependence of viscosity:

$$\eta_{sp}/c = [\eta] + K'[\eta]^2c. \tag{79}$$

For linear monodisperse polymers in a θ-solvent $K' = 0.5$; an improvement in the solvent leads to a decrease in K' and branching to an increase [72]. Therefore the presence of branching at a given K' is best judged by using a θ-solvent. For branched polymers of polystyrene [44,45], poly(vinyl chloride) [73], polybutadiene [74], polyacrylonitrile [75], poly(vinyl acetate) [76], etc. in corresponding "poor" and especially in θ-solvents systematic increasing in the values of K' are observed, whereas in "good" solvents this regularity does not always appear [77,78] and evidently is masked by the effect of polydispersity and volume effects. The relation between K' and branching has not been studied much theoretically, therefore this method remains purely qualitative.

It has similarly been shown [68,79] that the concentration dependence of the sedimentation constant of branched macromolecules is weaker than that of linear ones. An attempt has also been made to qualitatively characterise branching with the aid of the dynamo-optical constants of flow birefringence [59].

Determination of the polydispersity index M_w/M_n can also serve as a criterion of branching. However, the use of the value of M_w/M_n for a quantitative characteristic of branching is justified only in those instances where the branching reaction leads to the production of polymers with a given type of MWD, as for example, in the processes considered by Beasley [35], Stockmayer [31], or Bamford [37]. In the remaining instances when polymers are formed with $M_w/M_n > 2$ and it is known earlier that reaction take place leading to the formation of branched chains, use of the polydispersity index is possible only for qualitative and comparative estimates.

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The theoretical principles and experimental methods at present available permit in several instances a qualitative characterisation of the branching of various polymers. However, several problems need further attention. The principal ones are as follows: (1) the development of the theory of characteristic viscosity and of the coefficient of translational friction for branched polymers having an appreciable long-chain branching density; (2) the development of methods allowing long-chain and short-chain branching to be differentiated; (3) the synthesis and investigation of comblike branched polymers of known structure with long side-chains; and (4) a deeper study of polydisperse branched polymers.

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Lebedev All-Union Scientific Research
Institute for Synthetic Rubber,
Leningrad

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Acylation of Hydrazine and Its Substituted Derivatives with Derivatives of αβ-unsaturated Monobasic Acids

T.A.Sokolova and N.P.Zapevalova

The literature on the formation of hydrazides of αβ-unsaturated acids and also five-membered heterocyclic compounds in the interaction of hydrazine and its mono- and di-alkyl-substituted hydrazines with derivatives of saturated monobasic acids is reviewed. The properties and applications of these compounds are described.
The bibliography includes 97 references.

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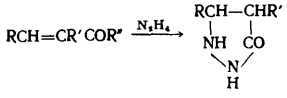
1. Acylation of hydrazine and monosubstituted hydrazines with αβ-unsaturated acids and their derivatives 1001
2. Interaction of αβ-unsaturated acid derivatives with asymmetrically disubstituted hydrazines 1003

1. ACYLATION OF HYDRAZINE AND MONOSUBSTITUTED HYDRAZINES WITH αβ-UNSATURATED ACIDS AND THEIR DERIVATIVES

Alkylhydrazines $RNHNH_2$ are known to be acylated at the NH_2 or NH group depending on the reagent used and the reaction conditions [1]. As a rule, when mild acylating agents (for example esters) are used and the system is cooled, monoacyl derivatives substituted at the NH_2 groups are formed [2-6]. Under more severe conditions, products of acylation at the NH group are obtained [3]. When monoalkylhydrazines are acylated with acid anhydrides [7,8], the products are acyl derivatives substituted at the NH group, while reaction with acid chlorides or heating with an excess of the anhydride yield *NN'*-diacylalkylhydrazines [9-11].

On the other hand, the interaction of hydrazine with derivatives of αβ-unsaturated acids usually leads to pyrazolidinones (I):[12]

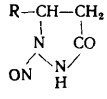


For this reason, the monomeric hydrazides of the majority of αβ-unsaturated acids have not been obtained until quite recently [13,14] and there are numerous contradictory literature data concerning the formation in this reaction of pyrazolidinones or hydrazides. For example, it has been stated [15] that phenylhydrazides of α-methyl and α-butylacrylic acids have been synthesised from their chlorides and phenylhydrazine. On the other hand, when the acids themselves were heated with phenylhydrazine, the products were 4-alkyl(ethyl or butyl)-2-phenyl-3-pyrazolidinones.

In the attempt to synthesise the hydrazides of other αβ-unsaturated acids pyrazolidinone derivatives were obtained†. Thus in the reaction of hydrazine hydrate with acrylic acid unsubstituted 3-pyrazolidinone is formed [15,17] while in the reaction of phenylhydrazine the product is 2-phenyl-3-pyrazolidinone [15,17,19]. Phenylhydrazine reacts with crotonic acid to form 5-methyl-2-phenyl-3-pyrazolidinone [18,20], while the reaction with ββ-dimethylacrylic acid gives 5,5-dimethyl-2-phenyl-3-pyrazolidinone [21,22].

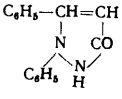
In 1963 Shvaika and Makarenko [23] described the preparation of the hydrazide of methacrylic acid by heating methyl methacrylate with hydrazine hydrate. However, it was found that in reality this results in the formation of 4-methyl-3-pyrazolidinone [24-28]. The infrared spectrum of this compound does not contain an absorption band corresponding to C=C stretching vibrations. Under the action of nitrous acid, the compound is converted [24,26] into 4-methyl-1-nitroso-3-pyrazolidinone and not into the azide of methacrylic acid. The formation of a coloured complex by the acyl derivative of this compound and a trivalent iron ion, recommended as a test for the hydrazide of methacrylic acid [23,29], is also a qualitative test for 3-pyrazolidinones [17,30]. The preparation of the hydrazide of acrylic acid by the reaction of methyl acrylate with anhydrous hydrazine has been reported [31]. However, on treatment with hydrochloric acid this substance too is converted into the hydrochloride of 3-pyrazolidinone, which suggests that it is not a hydrazide but a cyclic isomer.

Muckermann [32] described the preparation of hydrazides by heating crotonic and cinnamic acids with hydrazine hydrate. The products formed hydrochlorides and their reaction with benzaldehyde gave crystalline compounds to which the author [32] attributed to the structure of hydrazones. However, the reaction with nitrous acid gave *N*-nitrosopyrazolidinones (II) instead of the expected azides, which was accounted for by the cyclisation of the unsaturated hydrazides on treatment with nitrous acid [29,32-35]:



(II)

1,5-Diphenyl-Δ^4-3-pyrazolone (III) was obtained by heating cinnamic acid with phenylhydrazine [36]. The author suggested that the phenylhydrazide is formed initially and then cyclises and is oxidised by atmospheric oxygen:

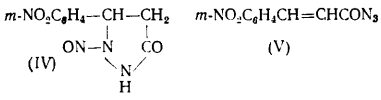


(III)

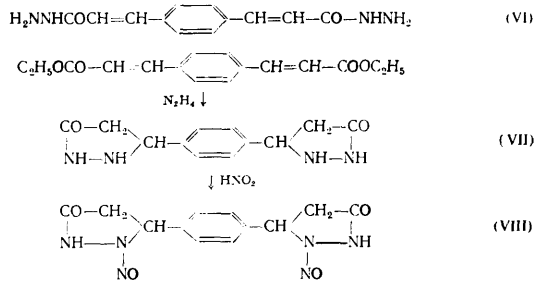
Two compounds were obtained on treating ethyl *m*-nitrocinnamite with hydrazine hydrate [37,38]. Both substances interacted with aldehydes and ketones and on this basis the author regarded them as different forms of hydrazides. However, one of these compounds, formed as the main product, is converted under the action of nitrous acid [38] into *N*-nitrosopyrazolidinone (IV) and the other (the side

†In the presence of oxygen, hydrazine can reduce the double bond of unsaturated acids [16].

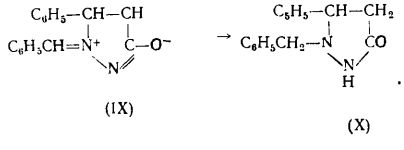
product) is converted into the azide (V), i.e. it is the acid hydrazide:



By allowing diethyl p-phenylenediacrylate to react with hydrazine hydrate in alcohol, Ruggli and Theilheimer [39] obtained a substance which was erroneously regarded as the dihydrazide (VI), although the structure of the bis-pyrazolidinone derivative (VII) was also considered for it. On treatment with nitrous acid, the substance is converted into the N-nitroso-derivative (VIII):

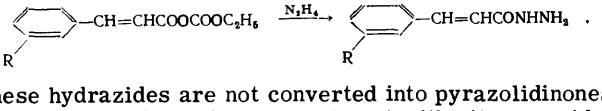


The formation of nitroso-derivatives under the action of nitrous acid demonstrates that the products of the reaction of $\alpha\beta$-unsaturated acids with hydrazine hydrate have the structure of pyrazolidinones [25-27,31]. However, a serious objection against this structure is the capacity of these compounds to condense with aldehydes and ketones. This contradiction was resolved by Godfredsen and Vangedal [40], who proposed the betaine structure (IX) for the product of the condensation of 5-phenyl-3-pyrazolidinone with benzaldehyde. On catalytic hydrogenation of this compound, one mole of hydrogen is absorbed and 1-benzyl-5-phenyl-3-pyrazolidinone (X) is obtained [40], which confirms the structure of compound (IX):



Later products of the interaction of 5-phenyl-3-pyrazolidinone with other aldehydes were also obtained [28,41].

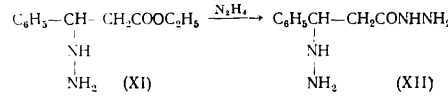
The hydrazides of cinnamic, m-nitrocinnamic, and p-nitrocinnamic acids have been obtained by the action of hydrazine hydrate on the mixed anhydrides of the corresponding acids with a carbonic ester:



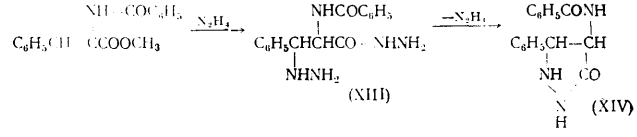
These hydrazides are not converted into pyrazolidinones on heating and yield azides on treatment with nitrous acid. It has been suggested [40] that the first stage in the formation of pyrazolidinone is the addition of hydrazine to the double carbon–carbon bond, which is followed by cyclisation to 3-pyrazolidinone.

The addition of monosubstituted hydrazine involves either the free or the alkylated amino-group of the hydrazine depending on the reaction conditions which results in the formation of 3-pyrazolidinone with substituents at the N_1 [24,31,40-43] or N_2 [15,18-22] nitrogen atoms.

The cyclisation is fairly slow and the hydrazine-ester formed initially, for example (XI), yields the hydrazide (XII) in the presence of an excess of hydrazine:



In the attempt to synthesise the hydrazides of α-benzoylaminocinnamic acid by the reaction of the methyl ester of this acid with an excess of hydrazine hydrate, Stodola [44] obtained the hydrazide (XIII) which on heating *in vacuo* was converted into 4-benzamido-5-phenyl-3-pyrazolidinone (XIV) with elimination of hydrazine. The benzamido-group was unaffected:



Hydrazides of unsaturated β-hydrazino-acids have also been obtained by treating esters of cinnamic and m- and p-nitrocinnamic acids with an excess of hydrazine hydrate [11,40,45].

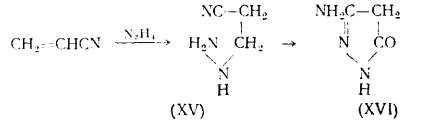
In a series of studies Deles and Polackowa [46-49] investigated the effect of the substituent on the rate of reaction and the yield of the product of the interaction of hydrazine with esters of ring-substituted cinnamic acids. When esters of cinnamic, m- and p-bromocinnamic, m- and p-nitrocinnamic, and p-methoxycinnamic acids were treated with hydrazine hydrate, a mixture of the β-hydrazino-ester, the hydrazides of the unsaturated and β-hydrazinodihydrocinnamic acids, and the corresponding pyrazolidinone was obtained. The authors established that the pyrazolidinones are formed by the cyclisation of the hydrazino-esters, but in the presence of an excess of hydrazine hydrate they are in turn capable of being converted with ring opening into the hydrazides of the β-hydrazino-acids.

Thus the first step in the formation of pyrazolidinone is the addition of hydrazine to the double bond of the $\alpha\beta$-unsaturated acid. Probably pyrazolone derivatives are formed similarly from esters of $\alpha\beta$-acetylenic acids [29,50,51]. This mechanism appears to be very probable [52], since the double bond in derivatives of $\alpha\beta$-unsaturated acids readily combines with nucleophilic reagents, including hydrazines [7,15-20,42,43,50-64].

The main chemical evidence in the determination of the structure of the products of these acylation reactions comes from their interaction with nitrous acid. Pyrazolidinones then yield N-nitroso-derivatives and hydrazides give the azides. In the hydrogenation of hydrazides over metallic catalysts one mole of hydrogen is absorbed with formation of saturated acids, while pyrazolidinones are not hydrogenated.

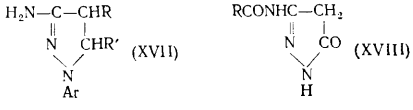
The most thoroughly investigated addition to an activated double bond is the interaction of nucleophilic agents (including hydrazines) with acrylonitrile. Several reviews have been published on the cyanoethylation reaction [52,54-57]. Hydrazine readily reacts with acrylonitrile yielding mono-, di-, tri-, and tetra-cyanoethylation products depending on the reaction conditions [7,57]. In the

presence of basic catalysts the β-cyanoethylhydrazine (XV) obtained cyclises to 3-aminopyrazoline (XVI):[7]



(XV) (XVI)

Substituted aminopyrazolines (XVII) were obtained by the cyanoethylation of phenylhydrazine in an alkaline medium and also by the reaction of phenylhydrazine with the nitriles of methacrylic, crotonic, or cinnamic acids[60,61]:



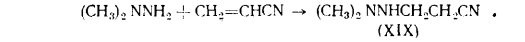
(XVII) (XVIII)

Acylhydrazines are also cyanoethylated at the amino-group both without catalysts and in the presence of acids[62,63]. In an alkaline medium the imino-group is probably cyanoethylated with subsequent cyclisation to the acylaminopyrazoline (XVIII). Monoalkylhydrazines react with the nitriles of αβ-unsaturated acids, forming derivatives substituted at the NH_2 or NH group[7,63] depending on the reaction conditions.

The interaction of derivatives of αβ-unsaturated acids with hydrazine and substituted hydrazines is nowadays widely used for the synthesis of pyrazolidinones[26-28,43,64-69]. It is also used for the identification of the products obtained in studies on other reactions.

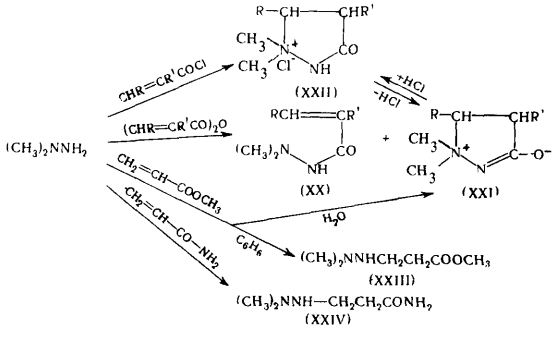
2. INTERACTION OF αβ-UNSATURATED ACID DERIVATIVES WITH ASYMMETRICALLY DISUBSTITUTED HYDRAZINES

Derivatives of αβ-unsaturated acids react with asymmetrically disubstituted hydrazines in different ways depending on the reagent and the reaction conditions. For example, dimethylhydrazine adds to the double bond of acrylonitrile[59] with formation of a monocyanoethylation product (XIX):



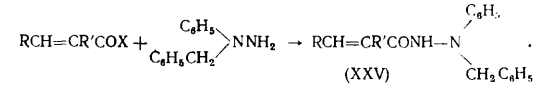
(XIX)

The action of the chlorides, anhydrides, and esters of αβ-unsaturated acids on asymmetric dimethyl- and benzylphenyl-hydrazines was investigated by Sokolova and co-workers[25,26,70-76]. The reactions of dimethylhydrazine with derivatives of αβ-unsaturated acids are represented by the following general scheme[26]:



where (a) R = R′ = H, (b) R = H and R′ = CH_3, and (c) R = CH_3 and R′ = H.

The products of the acylation of dimethylhydrazine with the anhydrides of acrylic, methacrylic, and crotonic acids are the dimethylhydrazides of these acids (XX) together with isomeric compounds (XXI) which the authors call 1,1-dimethylpyrazolinium 3-oxides[25,26,70,71]. When the chlorides of αβ-unsaturated acids are used, the salts (XXII), i.e. the hydrochlorides (XXII) of compounds (XXI), are formed[26,71]. The interaction of aqueous solutions of the salts (XXII) with anion-exchange resins yields the bases (XXI). The mode of the reactions of the esters of the same acids with dimethylhydrazine and the yields depend on the structure of the ester and the nature of the solvent. In polar solvents (water, alcohol) 1,1-dimethylpyrazolinium 3-oxide (XXI, a) is formed in almost quantitative yield from methyl acrylate and dimethylhydrazine, while the reaction with methyl methacrylate under the same conditions results in the formation of compound (XXI, b) in a much lower yield, which agrees with the lower activity of the C=C bond in the methacrylic acid ester[26,73]. In a non-polar medium or without a solvent dimethylhydrazine reacts with methyl acrylate, the product of addition to the double bond (XXIII) being formed. When an even weaker acylating agent (acrylamide) is used, the reaction with dimethylhydrazine yields only the product of addition to the double carbon–carbon bond (XXIV) regardless of the polarity of the medium[26]. On the other hand, in the reaction of the chlorides and anhydrides of αβ-unsaturated acids with asymmetric benzylphenylhydrazine cyclic compounds were not obtained. High yields of the benzylphenylhydrazides of the corresponding acids (XXV) were produced[26,72]:

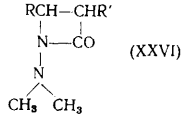


(XXV)

It is suggested[26,71,72] that cyclic compounds are not formed due to the screening effect of the bulky substituents at the nitrogen atom and the lower basicity of benzylphenylhydrazine compared with dimethylhydrazine, which hinders the nucleophilic addition of hydrazine to the double carbon–carbon bond[26].

The Structure and Properties of Hydrazine Alkylation Products

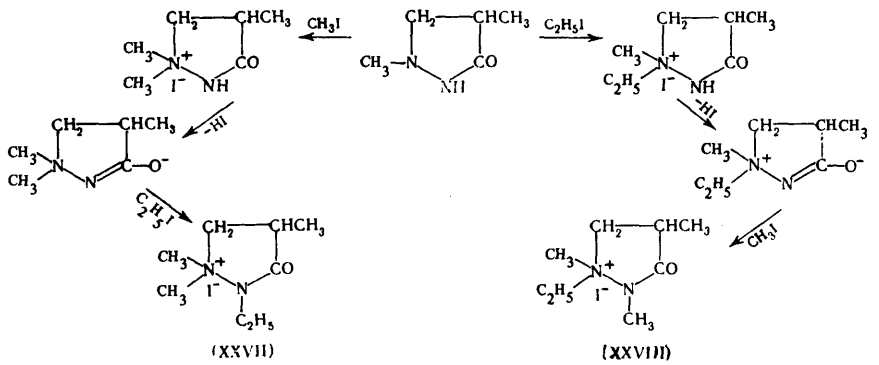
The interaction of dimethylhydrazine with derivatives of αβ-unsaturated acids is a method for the synthesis of the asymmetrically disubstituted hydrazides of these acids and also of a new class of heterocyclic compounds with a dipolar structure. On the basis of PMR spectra and studies of the hydrogenation products, the structure of *N*-dimethylamino-2-azetidinones (XXVI) was attributed initially to the cyclic isomers of the dimethylhydrazides[74,76]:



(XXVI)

However, it was subsequently shown by synthesis of pyrazolidinones of known structure[28] and also by the synthesis of various alkiodides and the study of their PMR spectra[26,74,75] that these compounds have the structure of compound (XXI).

Isomeric alkiodides (XXVII) and (XXVIII), which differ in the disposition of the methyl and ethyl groups at the nitrogen atom, were obtained by altering the order in which the initial 1,4-dimethyl-3-pyrazolidinone was methylated and ethylated [25,26]:



(XXVII) (XXVIII)

The crystalline alkiodides (XXVII) and (XXVIII), which have the same composition, exhibit different properties. With the β-lactam structure (XXVI) the same substance having all three alkyl groups at one nitrogen atom should be obtained regardless of the order of methylation and ethylation. However, the study of the PMR spectra of the alkiodides obtained showed [75] that two alkyl groups are located at one nitrogen atom while the third is at the second nitrogen atom.

The infrared spectra of compounds (XXI) show intense absorption bands in the region of 1580 cm^{-1}, which the authors assigned to absorption by the oxide group $-N=C-O^-$. [25,26,71] Such bands are also observed in the spectra of dipolar compounds with the linear structure (XXIX)‡ containing the group $N=C-O^-$: [77-80]

$$RCO\bar{N}-\overset{+}{N}(CH_3)_3 \leftrightarrow R\overset{O^-}{\overset{|}{C}}=N-\overset{+}{N}(CH_3)_3 \quad (XXIX)$$

In 1966 Wadsworth [65] synthesised several derivatives of pyrazolinium 3-oxides and called them, by analogy with Hinmann's compounds [77], cyclic amine-imides [65]. The pyrolysis of these cyclic compounds gave good yields of the dimethylhydrazides of methacrylic and crotonic acids [65]. Sokolova et al. [80] obtained by this procedure from 1,1-dimethylpyrazolinium 3-oxides the dimethylhydrazide of acrylic acid (XX, a), which is difficult to synthesise. Dimethylhydrazides of αβ-unsaturated acids are bases, like pyrazolinium 3-oxides, capable of combining with hydrogen halides and alkyl iodides [25,26,71]. The interaction of the methiodides of the dimethylhydrazides with bases (anion exchangers) results in the formation of the trimethylamine-imides of the corresponding unsaturated acids (XXIX). [78,80] The dimethylhydrazides of acrylic and methacrylic acids, their hydrochlorides, methiodides, and the trimethylamine-imides obtained from them are capable of polymerising in the presence of free-radical initiators with formation of high-molecular polyelectrolytes [81].

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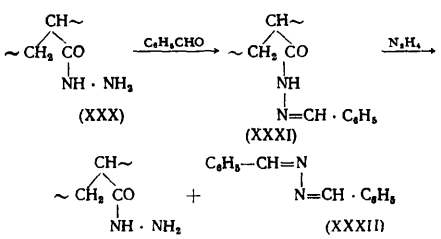
The interaction of arylhydrazines with derivatives of αβ-unsaturated acids [42,43,62,66-69,82-86] is one of the methods of synthesising "phenidones", i.e. 1-aryl-3-pyrazolidinones, which are important in photographic and cinematographic practice. They exhibit the properties of "superadditivity", increasing sharply the activity of hydroquinones in developing solutions [87-94]. 1-Phenyl-3-pyrazolidinone is used as a reducing agent in the determination of phosphorus in proteins [95].

Since the acylation of hydrazine is accompanied by cyclisation to pyrazolidinones, the preparation of unsaturated acid hydrazides is difficult and therefore Kern and coworkers [13,14] employed polymer-analogue reactions to prepare the polyhydrazides of acrylic and methacrylic acids. For this purpose, polyacrylic and polymethacrylic acid esters were treated with hydrazine hydrate. The polymeric hydrazides obtained in this way (XXX) are converted by treatment with aldehydes into polymeric hydrazones (XXXI) and can be used as "aldehyde-exchange" resins [14]. After the decomposition of the polymeric hydrazone (XXXI) with dilute sulphuric acid, the aldehyde may be re-isolated by steam distillation and the polymeric hydrazide is at the same time hydrolysed to polyacrylic acid. The polymeric hydrazone may be decomposed with hydrazine hydrate. Then the polymer is re-isolated as the hydrazide (XXX) and the aldehyde as the aldazine (XXXII): [14]



(XXX) (XXXI) (XXXII)

Polymeric hydrazones obtained by the interaction of polymeric acrylic hydrazide with aromatic hydroxyaldehydes may couple with diazo-compounds, forming polymeric azo-dyes with colours ranging from yellow to brown and brownish-black [14].

Polyhydrazides obtained by treating with hydrazine the copolymer of styrene and methyl acrylate have been proposed for the investigation of chain reactions and for use as polymeric soaps [29,96].

Polymeric hydrazides of methacrylic acid have been proposed as metal extractants. They form chelate complexes with nickel, cadmium, zinc, copper, and cobalt ions [97].

‡Hinmann [77] called such compounds trimethylamine-imides. This name cannot be regarded as sufficiently exact. Possibly these substances could be called *NNN*-trimethylhydrazinium *N'*-alkylidene-α-oxides.

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Institute of Macromolecular Compounds,
USSR Academy of Sciences, Leningrad

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Disperse Condensates of Metal Vapour

M.Ya.Gen and Yu.I.Petrov

This review deals with the role of associated complexes in the condensation and crystallisation of metals from their vapours. The presence in the metal vapour of polyatomic complexes (whether originally present or formed above the evaporation surface) is shown to have a significant influence on the initial condensation step on a solid surface or in an inert carrier gas. The mechanism of formation of highly disperse aerosol metal particles is discussed in detail. Some aspects of crystal and film growth from the vapour are briefly mentioned. 288 references.

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1. INTRODUCTION

Metal vapours are usually treated as monatomic ideal gases in studies of elementary crystallisation processes from the gas phase (preparation of aerosol particles, and growth of single crystals, whiskers, and films).

The possibility of formation of polyatomic complexes in the gas phase is often ignored. Yet, complexes of this type can be evolved during evaporation of a metal, or alternatively they can be formed by atomic collisions if conditions are favourable to the removal of the heat of condensation.

Since the condensation of a metallic vapour is essentially a non-equilibrium process, it is important to define the kinetic aspects of the irreversible dissipation of the energy of the colliding atoms. In principle, this energy can be dissipated by ternary collisions of the metal atoms close to the evaporation surface, or by ternary collisions involving atoms of the carrier gas, the excess of energy being eventually transferred to the walls of the vessel.

In an analysis of the elementary processes involved in the crystallisation of a metal from its vapour, it is important to include the irreversible dissipation of the energy of the condensing atoms and the subsequent growth and coagulation of the polyatomic complexes. This approach is gaining wide acceptance.

2. POLYATOMIC COMPLEXES IN REAL GASES

Many scientists (Boltzmann, Clausius, van der Waals, and others) have ascribed departures from ideal gas behaviour to the formation of associated complexes in real gases[1].

Much experimental evidence (both direct and indirect) is now available on the existence of these associated species in the vapour of practically all substances. Most of the work has concentrated on measurements of the partial pressure and dissociation energy of dimers. The results have been summarised in a number of reviews[2-6].

The analytical methods most commonly used to study the composition of the gas phase are the spectroscopic[2,3] and the mass spectrometric method[4], but other methods also have been applied: measurements of molecular velocities, measurements of the displacement of a molecular beam in a magnetic field, the magnetic resonance method, the torsional variant of the effusion method, and the beam density method.[5]

The dissociation energy of the dimer is usually referred to a temperature of 0°K, and is denoted by D_0.

D_0 values for approximately 40 elements up to Rn ($Z = 86$) are known at present. However, among the 23 transition metals the bond energy of the dimer is known only for nickel ($D_0 = 3.36 \pm 0.217$ eV).[7]

Drowart and Honig[4] showed that D_0 varies periodically with the atomic number Z. Verhaegen and coworkers[6] established a periodic dependence upon the atomic number Z of the ratio of the heat of evaporation of an atom at 0°K (ΔH_0) to the dissociation energy of the dimer D_0. All the existing data fall into three distinct classes, depending on the electronic structure of the element.

The relative equilibrium vapour pressure of the dimer (P_2) is given by the expression[6]

$$\frac{P_2}{P} = \text{const}\, e^{\frac{\Delta H_0}{RT}\left(\frac{1-\alpha}{\alpha}\right)},$$

where P is the vapour pressure of the monomer, R is the gas constant, T is the absolute temperature, and $\alpha = \Delta H_0/D_0$. If $\alpha < 1$, the concentration of the dimer decreases with increase of temperature. This is the case with molecules which are known to be stable at low temperatures (N_2, I_2, etc). For Bi_2, $\alpha \simeq 1$, and we can expect the relative amount of the dimer to be insensitive to temperature. Experimentally, the proportion of Bi_2 in the vapour shows a fast initial increase with temperature, reaches a maximum of ~45% in the region of 500°, and then begins to decrease slowly.[8] More recent measurements, however, suggest that the concentration of dimers may remain constant in the region 500–900°, since a vapour composition of 43% Bi + 57% Bi_2 has been reported[9] for 900°.

When $\alpha > 1$, as in the case of carbon and the metals, the proportion of dimers in the saturated vapour increases with temperature. Thus, for sodium vapour $P_2/P = 8.61 \times 10^{-4}$ at 127° and 0.25 at 727°; similar (though numerically smaller) values are obtained for Li and K vapours[5].

For Cu, Ag, and Au, $\alpha = 1.8 \pm 0.1$,[6] and the relative concentration of dimers in the temperature region 1300–1500°K is $(4-10) \times 10^{-4}$.[10] Other examples can be found in Nesmeyanov's monograph[5].

The vapours of some alloys (Ag–Au, Ag–Cu, Au–Cu,[11] and Ag–Sn, Au–Sn, Cu–Sn[12]) contain, in addition to atoms of the components, also symmetrical (Cu_2, Ag_2, Au_2, Sn_2)

and unsymmetrical dimers (AgAu, AgCu, AgSn, AuSn, AuCu, CuSn). The bond energies of these dimers are listed in Table 1.

These values are comparable to the dissociation energies of molecules such as Cl_2, Br_2, I_2.

Table 1. Bond energies of some metal dimers

Dimer	T, °K	D, eV	Literature reference	Dimer	T, °K	D, eV	Literature reference
Ag_2	1260—1360	1.63±0.03	10	AgAu	0	2.06±0.096	11
		1.9±0.3		AgCu	0	1.77±0.096	11
	0	1.78±0.10	13	AuCu	0	2.36±0.096	11
	0	1.63±0.096	11	AgSn	0	1.37±0.217	12
Au_2	1500—1610	2.18±0.03	10	AuSn	0	2.5±0.174	12
		2.3±0.3		CuSn	0	1.8±0.174	12
	0	2.30±0.12	13		1440—1560	2.02±0.03	10
	0	2.24±0.096	11			2.1±0.3	
Sn_2	0	1.99±0.174	13	Cu_2	0	2.21±0.11	13
					0	1.97±0.096	11

The bond energy D of the dimer can be simply related, in the case of hydrogen-like atoms, to the ratio of the ionisation potentials[14] of the given atom and of the hydrogen atom:

$$D = \frac{e^2}{4r_0}\left(\frac{I_X}{I_H}\right)^{1/2},$$

where e is the electronic charge (c.g.s.) and r_0 is the equilibrium separation of the atoms in the dimer. The extent to which this formula applies in practice is evident from Table 2.

Polyatomic complexes have been found to exist in many vapours. Thus, Miescher and Metzger[15-17] made the following observations in their study of the molecular complexity of vapours. Tellurium evaporates as Te_2 at 320°, selenium evaporates as 90% Se_6 and 10% Se_2 at 180°; arsenic evaporates as As_4 at low temperatures, as 70% As_2 + 30% As at 260°, and the vapour consists almost exclusively of As_4 molecules up to 530°.

According to Niwa and Yosiyama[18], selenium evaporates as an equilibrium mixture of Se_6 and Se_2, the proportion of Se_2 increasing from 12% at 185° to 25% at the boiling point. The presence of Se_2, Se_6, and Se_8 in selenium vapour near the boiling point has been inferred from measurements of the vapour density[19,20].

Early measurements[5] indicated that the vapour over liquid antimony consists of molecules containing 1, 2, and 4 atoms, whereas on approaching the boiling point the vapour consists mostly of dimers.

These results have been confirmed more recently by a mass spectrometric method[21], and some interesting features of the evaporation of antimony (both pure and from Au–Sb alloys) have been pointed out. Antimony vapour at ~550° consists entirely of Sb_4, whereas the vapour over an Sb–Au alloy contains Sb_2 and Sb in addition to Sb_4; at 950° the vapour contains 10% Sb and 25% Sb_2. On increasing the temperature from 800 to 1100° the concentration of Sb_2 and Sb increases by a few per cent because the concentration of Sb_4 decreases. The composition of the vapour is independent of the concentration of antimony in the alloy between 15 and 60%.

Searcy and coworkers[22], using the torsional variant of the effusion method, detected a large concentration of polyatomic molecules in silver vapour at pressures of 10^{-6}–10^{-4} atm. In the temperature range 1310–1420°K the effective molecular weight of the vapour was $M = 278 \pm 90$, corresponding to a molecular complexity of 2.56. The lack of agreement with Drowart and Honig's mass spectroscopic results[10] is probably due to a significant concentration of polyatomic complexes which escaped detection by the mass spectrometer. Korniev and Vintaikin[23] studied the sublimation of silver by combined radiochemical and mass spectrometric methods, and showed that (in contrast to evaporation from the melt[22]) evaporation from the solid involves exclusively monatomic species. Positive and negative polyatomic ions were detected in the mass spectra of Se, Te, Sb, and Bi vapours[24]. Mass spectrometric studies[25] of Ge, Sn, and Pb vapours revealed polyatomic complexes up to mass number ~400 at pressures of 5×10^{-6}–5×10^{-4} mmHg. The published plots make it clear that the predominant polymeric species in Ge vapour consists of 4-atomic groupings, whose proportion at 1300 and 1370° is 7×10^{-3} and 2×10^{-2} respectively of the number of single atoms.

Table 2. Dissociation energies of the dimers of some elements[14]

Dimer	$(I_X/I_H)^{1/2}$	r_0, Å	D, eV (observed)	D, eV (calc.)	Dimer	$(I_X/I_H)^{1/2}$	r_0, Å	D, eV (observed)	D, eV (calc.)
H_2	1.000	0.74	4.75	4.85	Sb_2	1.928	2.22	3.0—3.72	3.28
Li_2	0.630	2.67	1.05—1.14	0.85	Bi_2	1.966	2.38	1.72—3.62	2.97
Na_2	0.615	3.08	0.74	0.72	O_2	1.896	1.21	5.21	5.64
K_2	0.566	3.92	0.52	0.52	S_2	1.577	1.89	3.4—4.4	3.00
Rb_2	0.554	4.22	0.49	0.47	Se_2	1.505	2.16	2.37—3.55	2.52
Cs_2	0.536	4.57	0.45	0.42	Te_2	1.435	2.59	2.32—3.18	1.99
C_2	1.629	1.31	3.60—4.95	4.46	F_2	1.134	1.43	1.6—2.8	2.85
N_2	2.577	1.09	7.51—9.90	8.46	Cl_2	0.974	1.99	2.51	1.76
P_2	2.182	1.89	4.14—5.08	4.14	Br_2	0.931	2.28	1.99	1.47
As_2	2.071	1.91	3.99	3.90	I_2	0.876	2.67	1.56	1.18

In tin vapour the ions Sn_2^+ and Sn_4^+ were detected at < 1% concentration at 1200°; the ratio of ion currents for the evaporation of lead (~800°K) was $Pb_2^+/Pb^+ = 3 \times 10^{-5}$. Schissel[13] found a significant concentration of trimers and tetramers in Cu, Ag, and Au vapours.

Carbon vapour gives a large number of peaks in the mass spectrum[4,26,27], from which the partial pressures of C, C_2, C_3, ..., C_7 molecules have been computed up to 4000°K.[28] A large number of polymeric molecules was found in the mass spectra of C, Be, Mg, Ti, Fe, and Cu vapours generated in a high-frequency discharge[29]. Under these conditions, molecular ions up to C_{31}^+, Be_{25}^+, Al_{14}^+, Mg_5^+, Ti_5^+, Fe_6^+, and Cu_5^+ can be detected.

The dissociation energy of the complexes Bi_2, Bi_3, Bi_4, and BiPb has recently been determined mass spectrometrically[30].

Most workers are of the opinion that the polyatomic complexes appear in the mass spectrum as a result of the evaporation of organised groupings from the liquid metal. This opinion is based on the low probability of binary and ternary atomic collisions at low pressures of metal vapour (10^{-4}–10^{-5} mmHg) over a crucible or in a beam emerging from a Knudsen cell, and also on the pressure independence of the various ion current ratios[24,25]. Martynkevich[31,32] has stressed the correlation between the complexity of the vapour and the structure of the liquid metal. These views are confirmed by the effect of irradiation with thermal neutrons on the composition of indium vapour[33]: after

irradiation, the ratio of ion currents for dimers and monomers in the temperature range 773–1373°K increases by a factor of 15–50. The effect of irradiation persists for a long time (up to one year), but falls off rapidly if the sample is heated 50–100° above the working temperature.

Studies[34-40] of the mass spectra of gases escaping at supersonic speeds into a vacuum from an orifice are very relevant to the mechanism of formation of polyatomic complexes. Associations of ten or more molecules have been detected in molecular beams of many gases (Ne, Ar, N_2, O_2, CO_2, H_2O, NH_3, N_2O, C_2H_6, C_3H_6), and the complexes $ArCO_2$, Ar_2CO_2, $Ar(CO_2)_2$, etc. have been identified in molecular beams of CO_2–Ar mixtures. It is assumed that these associations must be present at equilibrium in the reservoir[34], or alternatively they must be formed during the adiabatic expansion of the gas[35,37-39]. On changing the pressure in the reservoir from 100 to 700 mmHg the mean number of molecules in N_2 associations increases from 160 to 6500, and the proportion of free molecules in the beam falls from 30 to 0.15%.[40]

These experimental findings indicate the presence of large numbers of polyatomic complexes in real gases. As a rule, these complexes do not generate a large partial pressure, they cannot contribute significantly to the observed pressure dependence of the low-temperature thermal conductivity and viscosity coefficients[41], and they have no effect on the formation of films on solid surfaces. The presence of molecular associations in moist air manifests itself in the absorption of ultrasonic energy[42]. Hence, no theory of gases can be satisfactory unless it makes allowance for the presence of associated complexes.

Mayer's group theory[43,44] was the first step towards a solution of this problem. This theory, based on the approximate evaluation of the partition function, treated a real gas as a rapidly changing assembly of non-interacting groups of 1, 2, 3... molecules.

Band[45], Frenkel'[46,47], and Vukalovich and Novikov[48,49] produced independently—and almost simultaneously—an approximate formulation of the complete functional dependence of the molecular weight distribution of the complexes upon pressure and temperature. Their theories rely on similar physical assumptions, which were most clearly stated by Vukalovich and Novikov as follows:

1. Molecular association is a basic process common to all states of a gas.

2. Association is caused by the van der Waals interactions between gas molecules. Because these forces are weaker than the chemical bonds holding simple molecules together, the latter retain their structure and their properties in the complex.

3. Complex formation occurs by the collision of at least three molecules; some of the colliding molecules combine into relatively stable aggregates, whilst the remainder take away the heat of condensation in the form of translational kinetic energy.

4. The associated complexes are assumed to be in thermodynamic equilibrium with the single molecules and to have the same translational energy. The average life-time of the complex is much greater than the duration of a simple molecular collision. Below the critical temperature of the liquid–vapour phase transformation the bond energy of the association is higher than the thermal energy, and the dimers are stable. As the size of the complex increases, the bond energy of each molecule within the complex also increases. As Tables 1 and 2 show, the bond energy of the dimers can be much higher than the thermal energy.

5. A real gas is treated as a mixture of simple gases, consisting of single molecules, dimers, trimers, etc. When the system is in equilibrium, the dissociation of the complexes in any of these gases is exactly compensated by the formation of the same complexes from the simpler species present in the other gases. These processes are entirely analogous to reversible chemical reactions.

Frenkel'[46,47] developed the theory of hetero-phase fluctuations, according to which the distribution of associated complexes is described by the general formula of fluctuation probabilities:

$$N_r \sim \text{const}\, e^{-\Delta\Phi(r)/kT},$$

where N_r is the number of complexes having radius r, and $\Delta\Phi(r)$ is the fluctuation in the thermodynamic potential of the gas resulting from the appearance of a complex with radius r. The calculation predicts a substantial proportion of aggregates containing upwards of 1000 molecules in the saturated vapour.

Ginnel[50] developed a theory of association from the concepts of chemical kinetics. Taking account of topological differences between complexes (linear and closed chains) he deduced a system of equations from which equilibrium constants for the growth and decomposition of the aggregates could be obtained by the matrix method.

Chakraverty[51] discussed the formation kinetics and the steady-state distribution of complexes over molecular weight by solving the stochastic problem.

The concentration of dimers in Ar, Kr, etc. at ordinary temperatures and pressures was found[52] to be approximately 0.1% by an approximate evaluation of the statistical integral.

Since the presence of associated complexes in any real gas is now experimentally established, it becomes imperative to re-examine the problem of liquid–vapour phase transformations.

We are not concerned here with a discussion of the classical theory of the condensation of a supersaturated vapour developed by Volmer and Weber[53] and by Becker and Döring[54] (VWBD), based on the concept of a critical nucleus arising in an ideal monoatomic vapour at some well defined critical supersaturation as a result of fluctuations. The many theoretical and experimental studies of this problem have been adequately summarised in review articles and monographs[55-60]. We shall confine ourselves to a few remarks.

The VWBD theory is unsatisfactory in that it attempts to apply Kelvin's equation to very small aggregates: the concept of surface free energy becomes meaningless when most of the atoms lie on the surface[61-63]. Studies of the thermodynamics of very small systems are continuing to attract attention[64-71].

Attempts have been made[72,73] to deal with polyatomic complexes within the framework of the VWBD theory. The kinetic equations[54] were generalised by including the attachment or removal of complexes as well as single atoms. Frisch and Willis[72] found that the probability of formation of critical nuclei in the vapour is increased by the presence of dimers. However, Katz and coworkers[73] reached the opposite conclusion. Dunning[74] found an analogy between Mayer's and VWBD's theories under certain conditions.

In any nucleation theory based on Mayer's approach, the Mayer groups must be indistinguishable from the real polyatomic complexes found in the supersaturated vapour. If the Brownian motion (both rotational and translational) of the droplets is ignored, this approach leads to an equation for the equilibrium concentration of critical nuclei which is identical to the corresponding equation in the VWBD theory[75].

According to Lothe and Pound[76], allowance for the translational and rotational motion of the polyatomic complexes increases the classical rate of homogeneous nucleation by a factor of 10^{17} (!). A lively polemic on this topic is in progress[77-83].

The VWBD theory fails to take account of the influence of an inert carrier gas. As Bradley points out[84], the theory is not applicable at high pressures, because the diffusion parameters (which play an essential role under these conditions) do not appear in the formula for the rate of formation of critical nuclei. Bradley shows by a thermodynamic argument that on increasing the pressure of inert gas the supersaturated vapour becomes undersaturated, and the rate of formation of critical nuclei falls to zero.

In the presence of equilibrium polyatomic complexes in the vapour phase we are compelled to re-examine critically both the concept of a vapour phase and the familiar concept of "supersaturation", which has hitherto been applied exclusively to a non-associated vapour. The problem is to define the maximum size of a complex which can be treated as part of the gas phase from the point of view of partial pressure, density, and therefore also degree of supersaturation.

On the other hand, it is not easy to define the size of complexes beyond which one must treat the phase as condensed.

On changing the pressure or the temperature of a vapour, the complexes adopt a new size distribution, and a macroscopic liquid is simply the largest drop within the given distribution of complexes. From this point of view, the concept of supersaturation has no clear meaning, since a pressure in excess of the equilibrium pressure of non-associated vapour does not give rise to a distinct new phase but simply alters the size distribution of complexes in the vapour.

It is important to stress the fact that all the statistical and thermodynamic theories of vapour condensation discussed above rely on equilibrium (reversible) models. Yet, the condensation of a vapour is essentially a non-equilibrium, irreversible process, governed largely by the problem of dissipating the energy of the colliding atoms.

In the presence of an inert gas or of solid surfaces, which can disperse the heat of formation of the polyatomic complexes, both the steady-state size distribution of the complexes and the overall process of homogeneous condensation may be profoundly affected.

The problems arising from the irreversibility of the condensation of metal vapour are further complicated by diffusion and convective currents in the carrier gas, and by the relatively large temperature gradients in the vicinity of the evaporation surface.

3. CONDENSATION OF METAL VAPOURS IN AN INERT GAS

Many experimental studies of the formation of aerosol particles from metal vapours in the presence of an inert gas have been published. The earliest attempt to formulate the quantitative aspects of the problem was made in 1912 by Kohlschütter and coworkers[85,86]. Volatile metals (Zn, Cd, Se, As) were slowly distilled in a vacuum or under various pressures of different gases (H_2, N_2, CO_2). The size and density of condensate particles formed on a known area of glass or quartz were studied under an optical microscope (56–300 × magnification). No significant differences were observed on varying the rate of evaporation or the position of the substrate. All the particles were approximately spherical; spherulites and dendritic crystals were occasionally found in the selenium condensates. The main conclusions of this work were:

1. As the gas pressure increases from 55 to 850 mmHg, the particle size decreases from ~0.1 to ~0.001 mm.

2. For equal pressures, the size of the particles and the density of the deposit depend on the nature of the gas. The average particle diameter decreases from H_2 to N_2 to CO_2.

3. In hydrogen the deposits are denser than in CO_2; mirror-like deposits are obtained in a vacuum and at very low gas pressures, and at atmospheric pressure the deposits are powdery, with large inter-particle separations.

These results have been treated in various monographs[87-89] as giving a true picture of the formation of aerosol particles. However, it is now obvious that only the large secondary conglomerations were detected in Kohlschütter's experiments. More recent (see below) electron-microscopic work reveals an entirely different picture of the relationship between the pressure and nature of the background gas and the disperseness of the primary aerosol particles.

Gen and coworkers[90] studied the condensation of sodium vapour in the presence of xylene and butadiene vapours. They developed an industrial method of production of organosols by high-frequency heating of the sodium directly within the liquid. The preparation of metallic sols by striking an electric arc in a liquid (proposed by Tikhomirov and Lidov[91] and realised by Bredig[92] and Svedberg[87]) is obviously another instance of the condensation of a metal vapour in the presence of the vapour of a liquid.

Aerosol particles of metals and oxides have been studied in the electron microscope for many years[93,94], and the first attempt to correlate the size of particles with the conditions under which the particles had been formed was made in 1948.[95] Gold was evaporated from a heated tungsten wire, in a nitrogen atmosphere, and the deposits were studied on a collodion film. For a constant rate of evaporation (3 mg s^{-1}), the smallest spherical particles (15–100 Å, average diameter ~40 Å) were obtained at a pressure of 0.3 mmHg, whereas at 1–3 mmHg pressure the particle size was 125–200 Å. On increasing the rate of evaporation from 0.5 to 15 mg s^{-1} (N_2 pressure 0.5 mmHg) the amount of material deposited increased very considerably but the mean particle diameter was unaffected. Small additions of oxygen to the nitrogen (1.32 mmHg N_2 + 0.08 mmHg O_2) had no effect on the electron diffraction patterns. However, the topographic structure of the deposit was altered, and the transmission of infrared radiation increased. This effect is ascribed[95] to condensation of the volatile tungsten oxide WO_3. A highly disperse gold deposit has been shown[96] to be an efficient absorber of infrared radiation, with very little reflection.

During the 1930's, Pfund had reported[97-99] that black condensates of Bi and Zn are obtained in an inert gas atmosphere or in a moderate vacuum. Levinstein[100] showed that the phenomenon is a universal one, and ascribed it to the formation of aerosol particles during condensation of a metal vapour in the presence of background gases. He showed that the appearance of the metal condensate on a collodion film under the electron microscope undergoes profound changes as the residual gas pressure is increased from 10^{-5} to 0.1 mmHg during evaporation. The deposits obtained under high vacuum conditions (~10^{-5} mmHg) consist of separate crystallites with a well defined shape (in the case of Zn, hexagonal platelets ~10^{-5} cm in

diameter), but on raising the pressure to 0.1 mmHg most metal condensates present a uniform appearance (a black film consisting of a large number of particles ~10^{-6} cm in diameter). The most unexpected result was obtained in the evaporation of Zn and Cd at the relatively high pressure of 0.01 mmHg: the resulting condensates had a surprisingly uniform structure and a specular surface. Levinstein explains these phenomena by pointing out that the metal vapour in the presence of residual gas is not atomic, but consists of a cloud of particles which are probably formed near the evaporation surface. When these particles land on the target they remain indefinitely on their adsorption sites and act as condensation centres. On the other hand, the adsorbed atoms can re-evaporate from the surface until they are eventually captured. Metal deposits (Au, Ag, Cu, Ni, Fe, Co, Cr, Mn, Ti, Be, Pb, Sn, Pd, Pt) give sharp electron diffraction lines when condensed in a high vacuum. On the other hand, condensates of those same metals obtained at a pressure of 0.1 mmHg give diffuse rings. The electron diffraction patterns of W, Ta, Ir, Nb, Rh, Ge, and Si show diffuse rings irrespectively of vacuum conditions during depositions. Levinstein concludes that the particles formed near the evaporation surface are essentially indistinguishable from the crystallites obtained on the surface of the substrate when a high-melting metal is evaporated (W, etc.), but the crystallinity of the former is less developed than that of the latter when the metal is low-melting (Au, etc.).

Bagguley[101] prepared aerosol particles of Ni, Co, and Fe, and of Fe–Si, Fe–Cr, and Fe–Ni alloys by striking a high-frequency arc between electrodes of the experimental material in a hydrogen atmosphere. Suspensions of these particles in paraffin oil were used in studies of ferromagnetic resonance.

Sheftal' and coworkers[102,103] showed that the films of Ge and Si deposited on single crystals of the same materials in a hydrogen atmosphere (760 mmHg) had better structural and electrical properties than the films obtained in a vacuum. This phenomenon, analogous to the formation of mirror-like deposits of Cd and Zn in Levinstein's experiments[100], is explained by postulating the deposition of Ge and Si aggregates from the hydrogen gas phase. Well formed and outwardly uniform silicon crystallites of 150–200 μm dimensions were shown by electron microscopy to result from particles ~300 Å in diameter.

Reshetnikov[104] studied the structure of thin films of Sb_2S_3 prepared by sublimation in a nitrogen atmosphere at pressures below 4 mmHg. He ascribes the highly disperse structure of the condensate to the formation of aerosol particles from vapour molecules which had lost their excess kinetic energy by collisions with nitrogen molecules.

Gen and coworkers[105] have examined the disperseness of aluminium aerosols as a function of formation conditions. A sample of aluminium was evaporated from a heated tungsten wire at the centre of a water-cooled glass bulb 8 cm in diameter. The bulb was filled with hydrogen, helium, or argon at 1–36 mmHg pressure. The deposits on the wall of the bulb were examined by electron microscopy: as the gas pressure was increased, the average size of the spherical particles increased gradually at first, but remained constant after reaching a critical value. The limiting particle diameter depends on the nature of the gas (~500 Å for He, ~700 Å for H_2, ~1500 Å for Ar). Depending on the disperseness, the colour of the films varied from black (for the finest particles, ~200 Å) to light grey (for condensates consisting of particles ~1500 Å in diameter).

Additional evidence has been published[106,107] in support of the view that the black deposits obtained by the evaporation of various metals (Au, Ag, Bi, Pb, Cd, Zn, Sb, Sn) in various gases (air, nitrogen, argon) at pressures < 0.5 mmHg consist of aerosol particles.

Rosinski and Snow[108] developed a model of the combustion of meteorites in the earth's atmosphere with formation of secondary aerosol particles by evaporating iron (using the exploding wire method) in argon, oxygen, and argon–oxygen atmospheres at pressures of $(1-4.1) \times 10^{-3}$ mmHg. The grid supporting the collodion film for electron microscopy was located in a side arm, where it was accessible to atomic aggregates only by diffusion. Aerosol particles ≤ 300 Å in diameter were formed at a pressure of 4.1×10^{-3} mmHg. Particles of iron oxide were obtained in an oxygen atmosphere. These workers used Smolukhovskii's coagulation theory to derive a system of differential equations describing the change in concentration of the various aggregates, and computed the size distribution of secondary particles as a function of time after the instantaneous evaporation of a meteor in the earth's atmosphere.

Karioris and coworkers[109-111] also described an aerosol generator based on an exploding wire, and prepared aerosols of various metals. Particles ~ 1000 Å in diameter were obtained in a nitrogen atmosphere. An X-ray diffractometer was used to show that under these conditions nitrides are obtained from Al, Fe, In, Ta, Th, V, W, and Zr. The Au, Ag, and Mo condensates contain practically pure metal. It was shown that explosion of Ag, Au, and Pt wires in air, and of Cu and Al wires in argon, gives aerosols of the pure metal, whereas explosion of base metal wires in air gives aerosols of the oxides. In addition to the fine particles (0.1–0.01 μm), relatively coarse particles resulting from the splash of the molten metal were detected.

Kimoto and coworkers[112] made an electron microscopic and electron diffraction study of the condensates of many metals (Mg, Al, Cr, Mn, Co, Ni, Fe, Cu, Zn, Cd, Ag, Au, Sn, Pb, Bi) obtained in the presence of various pressures of argon on a collodion film. They observed separate particles, both faceted and spherical, of size increasing from hundreds to thousands of Ångstroms as the argon pressure was increased from 1 to 35 mmHg. The aerosol particles in these experiments are assumed to be formed by condensation of the vapour on impurities. This view is hard to accept. If the impurities can act as condensation nuclei in the vapour more readily than the metals themselves, the mechanism is far from self-evident, particularly since the concentration of impurities in most of the metals was low, and yet aerosol particles were obtained in all cases.

Gen and coworkers[113] obtained spherical aerosol particles of Ag–Cu alloy, in which the solubility limits of the macroscopic alloys were largely exceeded, by the simultaneous condensation of the metal vapours in a gaseous carrier (Ar, He). The conditions for the formation of highly disperse alloys, and methods of determining their composition, are also discussed in that paper.

The problem of the origin of the atomic aggregates (whether emitted by the evaporation surface or formed above the evaporation surface) must be solved in each individual case. In 1914, Swann[114] had suggested that polyatomic complexes can evaporate from a metal in order to account for the electrical conductivity of thin metallic films. The assumption is to some extent confirmed by mass-spectroscopic measurements. Petrov and Rusin[115] obtained additional information in their study of the condensation of aluminium vapour on glass at ~ 10^{-3} mmHg

pressure. They inserted a copper screen with a circular orifice in front of their glass plate, and obtained a narrow concentric ring surrounding the central spot which could only be explained by postulating a double reflection of the particles from the plate and from the screen. The particles travel in straight lines, conserving the momentum acquired during evaporation. Electron microscopy showed that both the central spot and the thin surrounding ring consisted of particles ~ 30 Å in diameter. Evidently, evaporation of aluminium gives rise to polyatomic complexes as well as to single atoms, and the complexes add on further atoms during their flight. (This conclusion is consistent with the mass spectrometric measurements[29].) On raising the residual gas pressure from ~ 10^{-3} to 5 × 10^{-2} mmHg a highly disperse black powder appears on the screen but the deposit on the glass plate remains specular. This observation confirms Levinstein's observation that a mirror-like condensate can be formed from aerosol particles at a particular pressure of residual gas[100].

Palatnik and coworkers[116-118] studied the effect of temperature of the inert gas (argon) on the size and shape of the condensate particles of various metals (Pb, Sb, Cd, Zn, Mg) and their alloys. They evaporated the metals from an alundum crucible within an aluminium cylinder which could be heated to < 350°. The Mg, Cd, and Zn could be evaporated by an electric arc. The argon pressure was varied from 3 to 90 mmHg. The deposits were studied by electron microscopy and X-ray diffraction, and the results were treated by assuming two separate condensation mechanisms (vapour → crystal and vapour → liquid → crystal). The predominance of either mechanism is critically dependent on the temperature of the gas, controlled by the cylinder walls. However, the authors ignore the fact that at these pressures of argon the aerosol particles are formed near the evaporation surface, where the temperature is determined mainly by the crucible rather than by the cylinder walls. Hence, the published electron micrographs[116-118] are more characteristic of the coagulation and sintering processes of the particles on the heated walls of the apparatus than of homogeneous condensation.

Condensates from alloys[116-118] showed the following behaviour. Alloys of the eutectic type (Pb–Sb, Bi–Zn) gave a mechanical mixture of aerosol particles of the components. Condensates from solid solution showing continuous solid solubility (Bi–Sb, Cd–Mg) consist of particles covering a wide range of concentrations. In the remaining cases (Pb–Bi, Cd–Sb, Mg–Sb, Mg–Bi) the diffraction patterns suggest simultaneous condensation of the components on nuclei of definite compounds. At high enough crucible temperatures and for short evaporation times the composition of the condensate is exactly the same as that of the initial alloy. For example, with Pb–Sb and Pb–Bi alloys evaporated in 20 s the composition of the deposit becomes the same as that of the initial alloy when the temperature is raised to 1200°, and remains unchanged at still higher temperatures. This result would appear to need confirmation, in view of the large difference between the vapour pressures of the components of these alloys, and of the fact that the rate of arrival of atoms of the more volatile component from the bulk of the melt is not constant.

Gen and coworkers[119] prepared highly disperse Fe–Co alloys containing between 0 and 100% of Co by the aerosol method. The particles prepared in argon and helium at atmospheric pressure (~ 500 and ~ 160 Å in diameter respectively) were spherical. As the Co content was increased, the alloys gradually passed through a one-phase region (α-Fe structure), a two-phase region (α-Fe and γ-Fe), and a one-phase region (γ-Fe), finally adopting the Co face-centred cubic structure. The lattice parameters of the aerosol alloys are different from those of bulk alloys with the same composition. The lattice parameters of Fe–Co aerosol alloys and of Fe and Co particles were shown to be smaller than those of the corresponding bulk phases, and to be a function of particle size.

A study of the coagulation of silver aerosol particles of ~ 30–50 Å primary diameter has been published[120]. The metal vapour issuing from an induction furnace was allowed to mix with a stream of cold air at 23–68 mmHg pressure. The aerosol was led along a tube and electrostatically precipitated at various distances from the furnace. The extent of coagulation was obtained from the number of particles found in the deposit. The absolute concentrations were measured by a radioactive silver isotope.

Palatnik and coworkers[121] studied the size and shape of Mg, Cu, and Al particles deposited in an argon atmosphere on rods variously oriented with respect to the evaporation source. As the authors themselves point out, the interpretation of the results is complicated by secondary growth and sintering processes on the rods.

Japanese physicists[122-125] studied the crystal structure and geometrical form of the aerosol particles of various metals prepared in argon. Again it was shown that as the pressure is increased the particle size increases from ~ 100 Å (at 1 mmHg pressure) to several tenths of a micron (at 30 mmHg). Particles less than 300 Å in diameter were spherical, whereas the larger particles had a normal outline. Addition of 0.1 mmHg of air to 6 mmHg of argon produced particles with a rounded (Au, Ag, Fe, Pb) or abnormal (Zn, Cd, Mg, Be) outline. No oxides were detected on the surface of the particles. Surprisingly, it was found that chromium particles prepared in pure argon had an unusual structure (lattice constant of unit cube a_0 = 4.588 ± 0.001 Å), whereas chromium evaporated in an argon–air mixture (6 mmHg + 0.1 mmHg respectively) gave well formed particles with a normal body-centred cubic lattice (a_0 = 2.88 Å).[124]

The formation of aerosol particles with a pentagonal or, less frequently, hexagonal profile by the evaporation of gold and silver in argon (12 mmHg) is extremely interesting[126]. Particles of this shape had previously been observed in gold and silver condensed in a high vacuum[127,128]. Electron diffraction showed that the decahedral particles (giving a pentagonal profile) consist of tetrahedra bounded by {111} planes in mutually twinned positions. The expected small angle of misfit in the combination of five tetrahedra was not observed. The hexagonal outline is produced by icosahedral particles composed of tetrahedra.

The most detailed study of gold "compound particles" is due to Komoda[129]: some of his electron micrographs (obtained in a high-resolution microscope) are shown in Fig. 1. It is interesting to note that the decahedral and icosahedral shapes are found in particles ~ 20 Å in diameter, and are retained up to 150–200 Å particle size. Coarser particles have a more complex structure, but they are free from dislocations.

Wada made a comparative study[130] of the formation of Mg, Zn, Cd, Al, Fe, Cu, and Ag aerosol particles in helium and argon at pressures between 1 and 600 mmHg. His results are in qualitative agreement with the conclusions of Gen and coworkers[105]: particles are formed in a condensation zone whose width increases as the gas pressure is decreased; the particle size increases with gas pressure; for equal pressures, the particles are smaller and the condensation zone is larger in helium than in argon.

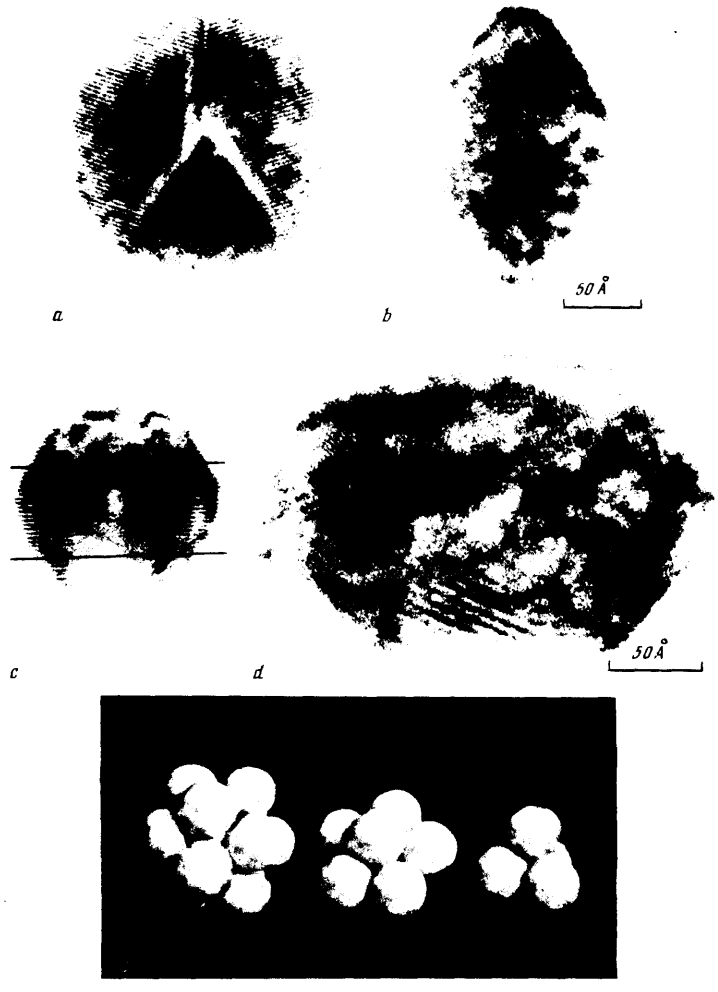

Figure 1. High-resolution electron micrographs of gold particles. The {111} planes are clearly visible. *a*) and *b*) show a small decahedral particle from above and laterally; *c*) is a small icosahedral particle with a hexagonal outline, the parallel straight lines are drawn to show the divergence of the lattice planes near the surface of the particle; *d*) is a larger particle of irregular shape, showing a complex internal structure; *e*) are models of the building of decahedral and icosahedral particles from the elementary tetrahedron

Particles of Fe–Co alloy of 100–700 Å diameter, prepared by evaporation in a low pressure of argon, are joined into long chains by magnetic forces[131].

Fukano and Kimoto[132] studied the structure of aerosol particles formed by evaporation of Ni–Pd, Fe–Ni, Au–Ni, and Ag–Pd alloys in argon. The particles had the same composition as the source alloy, and the composition dependence of their lattice parameter (face-centred cubic structure) was the same as for the bulk material within 2%. The aerosol particles of the Au–Ni alloy consisted of a solid solution which is normally stable only at high temperatures.

Highly disperse silver aerosols have recently been produced by evaporating the metal in argon and injecting the stream into cold air.[133]

The presence of an inert gas atmosphere enables new nuclei to be formed, and assists the coagulation of existing atomic complexes. On raising the gas pressure the average size of the metal aerosol particles initially increases to a limiting value, which is retained up to atmospheric pressure. This behaviour has an easy phenomenological explanation based on observations of fog formation. It is visually obvious that at high inert gas pressures the metal fog forms in a narrow region close to the vapour source: convective gas flow merely removes the particles from this "aggregation region", without appreciably affecting their size. When the gas pressure is lowered, the aggregation region widens, its inner boundary moves away from the evaporator, and its outer boundary moves closer to the

walls of the vessel. At the same time, the role of convective flow decreases and the role of diffusion increases. The mean particle size is affected by the gas pressure only when the outer boundary of the aggregation region reaches the wall of the apparatus. In this case the wall hinders the coagulation process which normally occurs in the bulk of the vapour–gas mixture.

No satisfactory explanation has yet been given of the limiting average particle size at high gas pressures or of the dependence of the limiting particle size on the nature of the gas [105,130].

The evaporated atoms come to thermal equilibrium with the gas very rapidly. According to Cravath's formula [134], the mean fractional loss of energy attending collisions between the atoms and the gas molecules is

$$f = \frac{8}{3}\frac{mM}{(m+M)^2}\left(1-\frac{T}{T_m}\right),$$

where m and M are the masses of the vapour atom and of the gas molecule respectively, T_m is the evaporation temperature of the atoms, and T is the gas temperature.

For example, in the evaporation of aluminium in argon $T_m \simeq 1800°K$, $T \simeq 300°K$, and therefore $f \simeq 0.53$, i.e. the energy of the atoms decreases by about a factor of two at each collision.

Rosin and Rabi [135] measured the mean free path of the evaporated atoms of alkali metals in various gases. From their results, summarised in Table 3, it is evident that the mean free path λ of the atoms is of the order of 1 mm at a gas pressure $P \simeq 10^{-2}$ mmHg. Hence, the atoms must come into thermal equilibrium with the ambient gas within a short distance from the evaporation source. Under these conditions, polyatomic complexes can be formed.

The effect of the complexes on the rate of evaporation of the metal has been studied [136]. The theoretical conclusion is that the diffusion layer of complexes which exists close to the evaporation surface in an inert gas atmosphere has no effect on the mass transport: hence, if the evaporation is limited by mass transport, the rate of evaporation is the same as for an atomic vapour.

Mizushima [107] tried to obtain a criterion for the formation of aerosol particles from the familiar expression for the number of atomic three-body collisions. Assuming that the higher complexes are formed by successive increments of single atoms, he obtained the approximate expression

$$\frac{Z_{n+1}}{Z_n} \approx \tau_n \frac{u}{\lambda},$$

where Z_{n+1} and Z_n are the numbers of collisions per second between atoms and complexes of $(n+1)$ and n atoms respectively; τ_n is the life time of the n-atom complex; u is the mean velocity and λ is the mean free path of the atoms.

Mizushima proposes the following inequality as the condition for the growth of particles:

$$\frac{Z_{n+1}}{Z_n} \geqslant 1, \quad \text{i.e.} \quad \tau_n \geqslant \frac{\lambda}{u}.$$

Taking $\lambda = 10^{-3}$–10^{-2} cm and $u = 10^4$–10^5 cm s^{-1} at $T \simeq 1000°K$, he obtains $\tau_n \simeq 10^{-7}$ s.

However, a growing particle must pass through the stage of association corresponding to a low value of n, for which $Z_{n+1}/Z_n \ll 1$. Hence, Mizushima's criterion is not realistic.

The most fruitful collisions are those between two atoms of the metal and a polymeric complex of the gas. Under these conditions the energy of combination of the atoms to give a dimer is transferred to internal degrees of freedom of the complex, which may undergo dissociation. Thus, the heat of condensation of the atoms can be dissipated without heating the gas. Dimers, trimers, etc. can then unite to give larger particles.

Table 3. Values of $P\cdot\lambda$ in units of 10^{-4} (P is the gas pressure in mmHg, λ is the mean free path of the metal atoms in cm)

Gas	Li, 860 °K	Na 700 °K	K 620 °K	Rb 590 °K	Cs 560 °K
H_2	16.2	8.30	5.44	4.24	3.20
D_2	18.6	8.74	5.85	4.65	3.65
He	22.6	12.52	8.32	6.50	4.89
Ne	22.5	10.94	7.77	6.65	5.41
Ar	11.4	5.90	4.22	3.75	3.34

Other conditions being equal, the size of the particles is practically independent of the rate of evaporation. This result suggests a relationship between the number of condensation centres and the rate of evaporation. The primary condensate particles (subcrystallites) can be bounded by close-packed crystal planes. For example, the smallest subcrystallite of a face-centred cubic metal is a tetrahedron consisting of four atoms and bounded by a family of {111} planes. Since the formation of a new layer on close-packed faces requires a high supersaturation [54,137], most of the atoms will be simply reflected from the close-packed faces of the subcrystallite. Hence, the formation of new subcrystallites (which can aggregate into aerosol particles by collision) becomes more favourable than the growth of existing subcrystallites at some stage in the dynamic condensation process. This seems to be the most likely explanation of the relative insensitivity of the aerosol particle size to the rate of evaporation. Strictly regular packing of the subcrystallites in the particle cannot be expected: some randomness in the mutual orientation of the subcrystallites is unavoidable. The molecular force field will have almost spherical symmetry, and the subsequent growth of the particle (by adding on more subcrystallites) will bear a similarity to the growth of a snow-ball. In practice, nearly all the metal aerosol particles examined in the writer's laboratory were found to be approximately spherical. Fig. 2 shows a crystalline particle of cobalt $\sim 10^{-5}$ cm in diameter photographed at high magnification ($\sim \times 300\,000$) in an electron microscope with ~ 10 Å resolution. The total absence of facets is obvious. Examples of the ordered grouping of tetrahedral subcrystallites in small gold particles (20–50 Å), and of the disordered grouping in larger particles ($\geqslant 150$ Å), are shown in Fig. 1.

The important role of subcrystallite coagulation in the formation of spherical aerosol primary particles, and in determining the size distribution in a given range of vapour concentrations, is stressed in a recent review by Fuks and Sutugin [138], and also by other workers [120,133,139].

In what follows we shall use the term subcrystallite to denote structural groupings of atoms ranging in size from the smallest possible unit cell to 20–30 Å, and bounded mainly by close-packed planes. X-Ray studies of phase transformations in aerosol particles have confirmed that their structure is subcrystalline [140,141]. Observations of ferromagnetic resonance in nickel, cobalt, and iron particles [142,143], and of plasma resonance in silver and copper

particles[144], and also of the temperature dependence of X-ray scattering[145,146], are consistent with this point of view.

Only a fraction of the subcrystallites, determined by the inert gas pressure, is able to coagulate in the gas volume: the remainder reaches the walls of the vessel. When these migrate over the surface of a solid, and experience the orienting effect of the substrate, they can give rise to well formed crystallites. The speed and direction of migration of the subcrystallites depends on their size, on the temperature and topography of the surface, on the presence of adsorbed impurities and external fields, etc.

Figure 2. Aerosol cobalt particle. Facets are completely absent though the particle has a crystalline structure

Most of the platelet-like crystallites so far obtained (Mg, Cd[112], and Zn[100,112]) by evaporating a metal in an inert gas atmosphere originated almost certainly at the surface. The grids and films used by Kimoto and coworkers[112,122] may have been heated quite significantly by radiation from the evaporation source, and this will have assisted the surface migration of subcrystallites. It has been shown[144] that silver condenses on a glass substrate 7 cm from the evaporator under 0.15 mmHg argon pressure in the form of islets consisting of a large number of sintered particles ~ 20 Å in diameter, whereas on removing the substrate to a distance of 15 cm coarser, isolated aerosol particles are obtained. The former deposits have a specular reflection, the latter are black. The black deposits exhibit plasma resonance under normal light incidence; the specular deposits do not, indicating a difference in electronic conductivity between the isolated and the sintered particles.

By suitable choice of evaporation conditions (gas pressure, position, and temperature of substrate), metal deposits of mixed origin can be obtained. An example is shown in Fig. 3, where a long chain of spherical particles held together by magnetic forces appears side by side with faceted particles of iron[112]. These chains are similar in size to the ferromagnetic particles of iron, nickel, and cobalt which are typical of condensates from the gas phase[119]. In a large enough vessel ($\geq$ 25 cm in diameter), and with an argon pressure of ~ 0.1 mmHg, spherical particles of most metals are usually obtained on the cold walls as condensates formed in the gas. These particles are sometimes amorphous (for example, aluminium[147] and bismuth[140]). However, larger particles ($\geq 10^{-5}$ cm) of low-melting metals can develop facets if their residence time in the hot gas is long enough. Kimoto and coworkers point out[112] that the lack of facets in particles less than a few hundred Ångstroms in diameter should not be dismissed as insufficient resolution in the electron microscope: it is an important aspect of the growth mechanism of the crystal. Under comparable preparative conditions, different metals give deposits with a narrow particle size distribution and approximately the same disperseness, but the higher-melting metals produce significantly smaller particles. Fig. 4 shows the integral and the differential size distribution of Bi, Pb, Sb, and Ag particles prepared by evaporating the metals from a hot tungsten wire in argon at 0.1 mmHg pressure in a glass bell-jar 25 cm in diameter.

Figure 3. Iron condensate on a collodion film, prepared in a magnetic field of ~ 1000 Oe under an argon pressure of 35 mmHg.[112] The faceted particles have grown on the surface of the substrate, whilst the chain of spherical particles must have been deposited from the gas phase

The actual colour of the macroscopic metal deposit gradually darkens as the particle size decreases. This trend is particularly noticeable with non-ferrous metals such as gold, silver, and copper. Complete oxidation of the particles produces a colour change. Thus, black powders of iron and lead develop the characteristic colour of the oxides (dark red and white, respectively) after being heated in air. The importance of the correct gas pressure during the preparation of the blackened sensitive areas of radiation detectors has been pointed out[148]: it is shown that a layer of black having reproducible optical characteristics can be prepared by evaporating Bi or Sb at 0.1–0.4 mmHg pressure.

The physicochemical properties of aerosol particles have been discussed in a number of papers, which we shall briefly mention below.

Harris and coworkers[149] discuss the sintering of gold aerosol particles. Gen and coworkers[147] studied the crystallisation of amorphous aluminium particles prepared under controlled conditions. Exposure of a photographic emulsion by the oxidation of aluminium particles (the Colson–Russell effect) has been observed by Petrov and coworkers[150–152]. The oxidation process, and the structural changes in the oxide skin surrounding aluminium particles, have been examined by Petrov and Bibilashvili[152]. Petrov made a detailed investigation of the thermal expansion, phase transformations, melt structure, and temperature dependence of X-ray scattering in aerosol particles of aluminium[146,151,153], lead[140,146,154], bismuth[140,146], antimony[140,146], nickel[145], cobalt[155], tin[141,146], silver[156], iron[157], and cadmium[158].

The optical properties of Al, Ag, Cu, and Se particles were investigated by Petrov[144]. Plasma resonance in Al particles, excited by fast electrons, has been discussed by Fujimoto and coworkers[159,160].

Gen and Petinov[161] studied electron paramagnetic resonance in lithium particles. Nuclear gamma-resonance was observed in particles of tin[162] and of an Fe–Ni alloy[163].

Petrov and coworkers measured the ferromagnetic resonance of nickel, cobalt, and iron particles[142], and also the magnetic and dielectric permeability of nickel suspensions in paraffin oil at a frequency of 9320 MHz.[143]

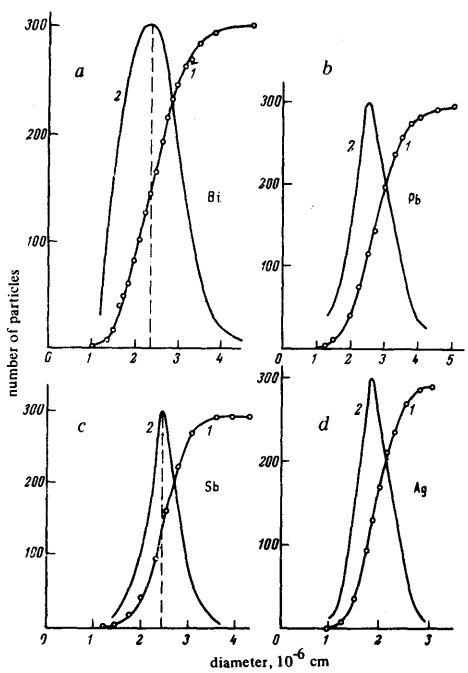

Figure 4. Size distribution of bismuth, lead, antimony, and silver aerosol particles prepared in a glass bulb 25 cm in diameter under ~ 0.1 mmHg argon pressure: *1*) integral distribution; *2*) differential distribution

The magnetic properties of Fe, Co, and Ni aerosol particles and of some of their alloys have been studied by several workers[131,164,165].

The hypothesis of a highly disperse structure of matter in the liquid and the solid state has been repeatedly proposed[166–183]. Experiments with aerosol particles are consistent with this hypothesis. Isolated subcrystallites, regularly assembled into a massive crystal, are assumed to be surrounded by a structureless (amorphous) layer of atoms which acts as an "inner lubricant". The thickness of the amorphous layers increases with temperature as a result of the "evaporation" of atoms from the surface of the subcrystallites, and this produces an increase in the rotational amplitude of the subcrystallites. At the melting point the subcrystallites enter a state of free random rotation: this is consistent with the appearance of an amorphous halo in the diffraction pattern of the liquid and with the vestigial structure of the original crystal found in the melt. The frequently reported "pre-fusion" of metals and associated specific heat anomalies[182–186], the increase in self-diffusion[187–189], and other phenomena[182] all point to a "loosening" of the bonds between subcrystallites[174] and to an increase in the thickness of the intervening amorphous layer. Lead particles ~ 200 Å in diameter close to the melting point have been shown to consist of approximately 115 face-centred cubic subcrystallites giving approximately 7 unit cells on each edge. On raising the temperature of the melt by 300° the size of the subcrystallites decrease only by a factor of 1.5.[154] It appears that the subcrystallites disappear completely only on approaching the critical temperature of the liquid–vapour transformation, when the melt adopts the uniform structure of a dense gas with the equilibrium distribution of polyatomic complexes. On cooling the melt, subcrystallites reform and gradually grow in size. Finally, the subcrystallites begin to touch one another, and an ordered array becomes energetically more favourable: in other words, the melt solidifies. The phase transformation is an avalanche-like cooperative process. The most convincing proof of the subcrystallite structure of aerosol particles is obtained by direct electron microscopy[126,129] (Fig. 1), and also by observing the anomalies in the coefficient of expansion of Al, Pb, Ag, and Cd particles close to the melting point.[158]

This secondary, disperse structure of matter in all three states of aggregation is due to kinetic processes on an atomic scale which are almost impossible to avoid in practice. Even carefully grown crystals exhibit a secondary structure in spite of the fact that an ideal single crystal of unlimited size is thermodynamically favoured. Thus, Delisle and Davis[190] observed a fine structure of particles ~ 1000 Å in diameter in copper crystals grown from the melt within the familiar mosaic blocks.

In some cases, crystals grown from the vapour in an inert gas atmosphere develop as a regular array of aerosol particles, especially when the latter show a narrow size distribution. Layer growth and dendritic growth of crystals can be explained by this mechanism.

It was pointed out long ago[191,192] that the thickness of layers at crystal faces is comparable to the size of the elementary cell (i.e. is larger than atomic dimensions, in contrast to the requirements of the dislocation theory). Growth steps up to ~ 1000 Å high[192] present insurmountable difficulties to the dislocation theory. Frank[193] was forced to postulate an empty channel at the centre of a dislocation with such a large Burgers vector: the function of this channel is to relieve the concentration of elastic energy which would otherwise exceed the mechanical strength of the material. No experimental evidence of the existence of this channel has yet been produced.

Spiral steps 0.1–1 μm high have been observed on the surface of various crystals (copper[194,195], lead[196], cadmium[197], germanium[198], silicon[199]). These are clearly associated with atomic groupings rather than with single atoms.

Sears[200] ascribes the formation of screw dislocations with a large Burgers vector to the collision of a growing ideal crystal platelet with an obstacle in the form of a colloidal particle. Lang[201] showed that random growth "faults" in the early stages of the formation of a step must result in a continuous spiral step of indeterminate height rather than in a circular step.

Evidently, subcrystallites or small aerosol particles of approximately uniform size can be packed as parallel layers on a growing solid surface, whereas the larger

particles or surface defects can provide the obstacles postulated by Sears and Lang to explain the large growth spirals found in crystals.

Straumanis[202] made the first experiments on the growth of Mg, Zn, and Cd crystals from the vapour in an inert gas (hydrogen) atmosphere. The metals were evaporated within a glass tube along which a temperature gradient was imposed. Well faceted crystallites up to a fraction of a millimetre in size were obtained under suitable conditions of hydrogen pressure and evaporation temperature. For hydrogen pressures above some well defined limit (~ 4 mmHg for Zn), platelet-like Zn and Cd crystals were grown. Mg gave loosely adherent thick layers when the pressure was raised to 0.5 atm. Thin layered Cd crystals were formed at hydrogen pressures of the order of 1 atm. The growth of metal crystals from the vapour in an inert gas atmosphere is discussed in a number of papers[203-208]. Keepin[203] studied the growth of Cd and Zn crystals from the vapour as a function of the evaporator temperature (molybdenum crucible), substrate temperature (Ag for Cd, Cu or Ni for Zn), and pressure of purified nitrogen (between 10^{-5} and 760 mmHg). Large but imperfect crystallites were obtained at nitrogen pressures > 0.5 mmHg. Dendritic crystals were predominant in the pressure range 10^{-2}–10^{-1} mmHg and substrate temperatures 250–350° (for Cd) and 200–350° (for Zn). Under the conditions listed in Table 4, large and well developed hexagonal crystals were grown. Under still lower pressures, and substrate temperatures close to room temperature, a few dendritic crystals were obtained but the deposits were predominantly amorphous (particle size ~ 100 Å, estimated from the X-ray line widths).

Table 4. Optimum conditions for the growth of Cd and Zn single crystals from the vapour in a nitrogen atmosphere[203]

Metal	Evaporator temp., °C	Partial vapour pressure, mmHg	Substrate temp., °C	Nitrogen pressure, mmHg
Cd	310–321	$\sim 10^{-1}$	305±3°	10^{-2}–$5\cdot10^{-2}$
Zn	409–419	$\sim 2\cdot10^{-1}$	410±3	10^{-2}–$3\cdot10^{-2}$

Keepin suggests that the removal of the heat of crystallisation is affected by the pressure dependence of the convective flow of inert gas: as a result, the shape and size of the crystals growing on the substrate by the addition of single atoms show a considerable variation. Coleman and Sears[204] studied the influence of inert gases on the growth of Zn, Cd, and Ag from the vapour. Filamentary growth ("whiskers") was observed in the presence of hydrogen or helium at 10–600 mmHg pressure. The whiskers were formed both on the growing Zn crystals and on the glass or quartz substrates. Some individual whiskers were up to ~ 17 mm long and 1–3 μm in diameter. The diameter of the whiskers decreased with increase of gas pressure, reaching a few tenths of a micron at 600 mmHg hydrogen pressure. Coleman and Cabrera[205] observed Zn and Cd whiskers 1–2 mm long and 1–10 μm in diameter, grown from the vapour in an inert gas at atmospheric pressure.

Price[206] grew Cd crystals from the vapour on a quartz fibre in an argon atmosphere. The temperature T and degree of supersaturation η were calculated at all points along the fibre, and a critical value ($\eta \simeq 0.4$) was noted below which no crystals grew. For $\eta \leqslant 2$, thin platelets and whiskers grew together on the filament irrespective of T and η; for $2 \leqslant \eta \leqslant 10^2$ thick hexagonal platelets were obtained; branching dendrites appeared and grew to a large size for $\eta \geqslant 10^2$ and $T \leqslant 250°$. Cd and Zn crystals have been grown[207,208] from the vapour in 10–600 mmHg of argon on the wall of a glass tube. Both platelet-like microcrystals and whiskers (up to 10 mm long and 1–5 μm in diameter) were obtained.

In all the work mentioned above[202-208] the rate of growth is assumed to be determined by the diffusion of atoms in the inert gas, and controlled by the degree of supersaturation of the vapour. The formation of aerosol particles, and their combination to give microcrystals, are ignored in spite of the fact that most of the evaporated material must have passed through the stage of aerosol condensates at the inert gas pressures used in this work. Aerosol particles are formed in all systems where crystallisation from the vapour phase is assisted by chemical reactions such as transport reactions and vapour-phase reactions[209,210]. This factor must be considered when analysing the mechanism of the process.

4. MECHANISM OF CONDENSATION OF A METALLIC VAPOUR ON A SOLID SURFACE

The primary stage in the formation of a metallic condensate on a solid surface is a very complex problem with many controversial aspects. Most workers (see previous reviews[57,211-213] and some more recent papers[214-221]) correlate the structure of condensed metal films exclusively with atomic processes at the substrate surface. The role of polyatomic vapour complexes is completely ignored.

Two different explanations have been put forward for the formation of small particles in the early stages of film deposition: they can be termed the "gradual" and the "spontaneous" nucleation mechanism respectively[222]. During "gradual" nucleation of particles the atoms of the deposit move over the substrate until they have lost their thermal energy and become attached at random or at preferred surface sites. "Spontaneous" nucleation of particles occurs in the amorphous or quasi-gaseous state at some critical concentration of deposited material.

According to Semenov[223], adsorbed atoms can be treated as a "two-dimensional" vapour which condenses on reaching some critical supersaturation.

Some of the earliest workers[224-230] had noted the existence of a critical surface temperature T_{cr} above which the metal vapour will not condense. T_{cr} was shown to be a function of the density of the molecular beam. Frenkel[231] put forward an explanation, involving the adsorption of all the impinging atoms, by further developing Langmuir's ideas[232]. If two atoms combine into a dimer during their life time in the adsorbed state, the latter can act as a centre for further condensation of atoms because the probability of secondary evaporation is lower for polyatomic surface species. However, at low beam densities the dimer can dissociate before the attachment of a third atom: obviously, in this case no film is formed. Because of the clear physical picture offered by Frenkel's theory, various modified theories were subsequently based on it.[57,212] On the other hand, the experimental fact that T_{cr} varies with time[233,234] lies outside the scope of this theory. Furthermore, theoretical calculations[235-237] suggest that metal atoms should always be adsorbed on a solid surface at all

experimentally accessible evaporation temperatures. Yet, supersaturations of $\sim 10^{15}$ or more are often needed in molecular beam experiments to induce significant condensation. Sears and Cahn[242] tried to resolve this drastic shortcoming of the theory of surface film nucleation by postulating a slow transfer of energy for atoms in the adsorption layer. According to these workers, the temperature of the layer must be intermediate between those of the substrate and of the evaporator. By modifying Frenkel's theory they concluded that for a constant beam intensity and a fixed substrate temperature there must be a critical evaporation temperature above which no nuclei are formed on the substrate.

Hudson[243-245] studied the formation of Zn, Cd, and Se crystal nuclei on glass and noted large discrepancies between the observed rates of condensation and those predicted by the classical theory. His explanation is analogous to that of Sears and Cahn[242], since he assumes a temperature of the adsorbed layer of condensate intermediate between the substrate temperature and the evaporator temperature.

However, Shade's experiments[241] with a cadmium molecular beam condensing on polyethylene films have shown convincingly that the results are independent of evaporator temperature, and hence that the theory of Sears and Cahn is incapable of explaining the enormous supersaturations ($\sim 10^{17}$–10^{20}) needed to initiate condensation.

Evseev and Ozhegov[246] have recently shown that for a fixed density of the molecular beam T_{cr} increases with beam temperature, whereas for a fixed substrate temperature the critical beam density decreases with increase of beam temperature. These results are not inconsistent with Shade's conclusions, since (as the authors themselves point out) the antimony vapour in their experiments probably consisted of 4-atomic complexes which could have dissociated on collision with the substrate. Gretz[217,220] tried to explain Hudson's experiments[243] on the condensation of Zn vapour on glass by refining the classical fluctuation theory of heterogeneous nucleation[76,247]. He introduced into the expression for the free energy of formation of a cap-shaped nucleus a term for the linear tension along the interface with the substrate. However, the theory of Gretz, like other variants of the classical theory based on the Gibbs–Kelvin equation, is not applicable to very small nuclei.

The very low observed rates of formation of Zn nuclei on glass and on mica[243] can be ascribed to a low thermal accommodation coefficient $\alpha_T = (T_0 - T_a)/(T_0 - T_S)$, where T_0, T_a, and T_S are the temperatures of the beam, the adsorbed atoms, and the substrate respectively.

If full thermal accommodation of the atoms is not achieved (i.e. $\alpha_T < 1$), the adsorbed layer will be at a higher temperature than the substrate, and the real supersaturation (η_a) will be correspondingly lower. Gretz attempted[219] to evaluate α_T from experimental data for η_a without resorting to the detailed equations of the theory of nucleation. He started from an empirically established linear relationship[57] between $\ln \eta_c$ and $(1/T_S)$, where η_c is the apparent critical supersaturation defined as the ratio of the effective vapour pressure in the beam to the vapour pressure corresponding to T_S. Assuming α_T independent of temperature, he postulated that $\ln \eta_a$ must also be linear in $(1/T_S)$, i.e. that the condition $\partial^2 \ln \eta_a / \partial (1/T_S)^2 = 0$ must obtain. In spite of these arbitrary assumptions, he obtained the reasonable values $\alpha_T = 0.993$ and $\alpha_T = 0.998$ for the condensation of Zn on glass[243] and on mica[248] respectively.

Hirth and coworkers[249] explain the discrepancy between Hudson's results[243] and the theory by pointing out that at low supersaturations stable nuclei are more likely to be formed by collisions between nuclei of subcritical size than by the addition of single atoms to critical nuclei.

Moore[250] has reviewed recent work on the condensation of metals on solid substrates using emission and electron microscopy. He also concluded that small atomic groupings have a high mobility which allows them to coalesce like liquid drops. Gretz observed[218] the sudden formation and the rapid growth of a silver nucleus in the emission microscope. Curzon and Kimoto[251] studied the condensation of lead vapour on molybdenite in an electron microscope, and observed an ordered deposition of small drops on surface microdefects of the substrate, which was heated to 350°. Ciné-photography was used to demonstrate the high mobility and the coalescence of the drops. The Brownian motion of 20–30 Å gold crystallites prepared by condensing the vapour on a KCl slip in a vacuum of 8×10^{-9} mmHg has recently been demonstrated experimentally[252].

Walton tried to resolve the uncertainties which arise when the concept of surface energy is applied to very small particles. He derived[253,254] a formula for the frequency of formation of nuclei in terms of the density of adsorbed atoms, the heat of adsorption of an atom, the dissociation energy of the critical nucleus, and the activation energy for surface diffusion. According to his model, configurations of two, three, etc. atoms on the substrate remain in stable equilibrium with the vapour phase until the critical supersaturation characteristic of each configuration is reached, when the shape of the nucleus suddenly changes. This theory was applied to the growth of oriented layers[255,256]. The possible orientation and the shape of the atomic groupings formed on a crystalline substrate by vapour condensation have been discussed theoretically by Halpern[216].

The growth of single-crystal films is a very complicated problem. The quality of the film depends on many factors, often inadequately controlled (e.g. the background pressure of residual gases). Background gases can affect the kinetics of the process both in the gas phase and at the surface of the substrate. For example, changes in structure and texture formation are observed on changing from a low vacuum ($\sim 10^{-2}$ mmHg) to an ultra-high vacuum ($\sim 10^{-9}$ mmHg) in the condensation of Au, Ag, Ni, and Al films[257]. There have also been reports of residual gas effects on the properties of condensed films of tin[258,259] and indium[260].

Palatnik and Komnik studied the structure of condensates (Bi, Sb, Pb, Sn, and other metals) on a glass plate which was heated non-uniformly[213,261-263]. They noted a sharp discontinuity in the optical transmission of the deposits at a substrate temperature (T_n) approximately 2/3 of the melting point of the metal, which they ascribed to a difference in the size and number of particles on either side of this transparency boundary. This difference in the structure of the condensate is explained by different condensation mechanisms, assuming that the supersaturated "two-dimensional" metal vapour condenses by a vapour → liquid → crystal mechanism on the hot side of the substrate and by a vapour → crystal mechanism on the cold side.

Fisher and Anderson[264], in a recent study of the condensation of lead, showed that T_n can change from 189 ± 2° to ~ 245° whilst the residual gas pressure remains below 10^{-5} mmHg. They also showed that the difference in structure of the deposit on either side of the transparency boundary lies mainly in the development of facets and not (as had been assumed by Palatnik and Komnik[261-263]) in the

size and number of the particles. At substrate temperatures above T_n the particles of the deposit are almost spherical, with rudimentary facets, whereas at substrate temperatures below T_n the particles are elongated with well developed facets. Fisher and Anderson were critical of Palatnik and Komnik's double condensation mechanism, and they proposed their own explanation of the difference in structure shown by lead condensates. Quoting some calculations by Burton and coworkers[137], they assume that different facets of the lead crystallites melt at slightly different temperatures: in this way, the crystal habit of the particles becomes a function of the substrate temperature. Fisher and Anderson's arguments also explain the experimental fact that T_n is independent of film thickness[261-264].

Many of the problems raised by the initial stage of formation of metallic condensates become clearer when allowance is made for the possible adsorption of polyatomic aggregates from the vapour. These have a longer life time in the adsorbed state than single atoms, and hence they can act as primary condensation centres. It can be assumed that at high substrate temperatures only the larger complexes are retained on the surface, whereas single atoms and small associations are either reflected or rapidly re-emitted from the surface. On this model, it is not difficult to explain the existence of a critical temperature for the condensation of a vapour on a solid surface, its dependence on time and on the density of the molecular beam, and also the structural differences observed when the substrate temperature is non-uniform.

Many experimental observations provide direct evidence for the deposition of quite large particles (although rapid growth of the primary adsorbed polyatomic complexes cannot be entirely dismissed).

Thus, when the condensation of Cd and Zn molecular beams on a Formvar substrate is observed directly in the electron microscope[265], primary particles up to ~ 200 Å in size appear quite suddenly. Newman and Pashley[266] made an electron diffraction study of the condensation of copper vapour on silver, and detected the sudden appearance and subsequent rapid growth of oriented primary crystallites ~ 60 Å wide and ~ 12 Å thick. Particles ~ 100 Å in size, mostly concentrated along step edges, are observed when defects in freshly cleaved NaCl and KCl surfaces are decorated by vacuum sublimation of Au, Pd, Pt, and Ge on the heated substrate surface. In spite of the large difference in the numbers of particles found on the smooth areas and on the step edges of the surface, the particle size is approximately constant. Furthermore, gold particles deposited on glass and on small NaCl crystallites previously sublimed on the same glass surface are of practically uniform size, despite the fact that the concentration of particles is approximately 10 times higher in the former case[268]. These results are not easy to explain in terms of the growth of particles by surface migration of adsorbed atoms, since that mechanism predicts an inverse relationship between the size of the particles and their concentration (assuming a uniform density of the molecular beam).

The finely grained films obtained at low substrate temperatures are particularly interesting. During the 1930's, Kramer[271-273] prepared thin (~ 10^{-4} cm) amorphous films of a large group of metals (Fe, Ni, Pt, Zn, Sn, Cd, Sb, Ir, Al, Pb, Hg, Mo) by condensing their vapour on a glass surface cooled in liquid air using thermal evaporation or cathodic sputtering in a low pressure of hydrogen. When the deposits were heated above some well defined critical temperature their electrical properties showed a sudden, irreversible change, approaching the properties of the bulk metal. Kramer suggested that the metal atoms lose their kinetic energy by collisions with gas molecules, and are therefore unable to combine with the crystal lattice when first adsorbed on the surface. However, polyatomic complexes and subcrystallites must have been present in his experiments. At low substrate temperatures, these are not mobile enough to combine into ordered single-crystal blocks.

Gen and coworkers[274] studied the electron diffraction patterns of Fe, Ni, Cd, and Hg deposits (and also the electrical conductivity of Cd deposits[88]) prepared in a high vacuum on a glass surface at liquid-nitrogen temperature, and found a crystalline structure with a crystallite size of ~ 10^{-7} cm. These layers underwent recrystallisation on being heated, as shown by the sharpening of the diffraction lines and by the irreversible decrease (by a factor of 2–2.5) in electrical resistance[88].

Later work confirmed the conclusion of Gen and coworkers[274] that low-temperature condensates are apparently amorphous only because of the small size of the primary crystallites of which the film is composed.

More recent electron-diffraction studies[275] of Bi, Ga, Be, Fe, Cr, and the Pb–(12% Bi) alloy, condensed at 4.2°K, has revealed a similarity in radial distribution function between atoms in the films and atoms in the corresponding bulk melts. The size of the primary subcrystallites is estimated to be only a few Ångstroms. On raising the temperature to 77°K the films are converted from an amorphous into a crystalline structure, with a crystallite size of the order of tens of Ångstroms. The same author[276] demonstrated the amorphous structure (subcrystallite size of the order of Ångstroms) of Ti, Mn, Co, Pd, Y, and Fe–Ni, Ag–Cu alloy films condensed in a high vacuum on a cooled substrate (77°K).

Grigson and Barton[277] have reviewed existing electron diffraction calculations for very small crystallites, and have developed a method of evaluating the Debye interference function for an assembly of identical, randomly oriented face-centred cubic subcrystallites containing from 2 to 9 atoms on an edge. By comparing the calculated diffraction patterns of liquid lead and of thin films of Pb, Ag, and Fe, it was shown[278] that the aggregates form an amorphous structure similar to that of a monoatomic liquid during the early stages of film growth (up to 10 Å).

Measurements of the line width in electron diffraction patterns of Cu, Al, Ti, Pb, Sn, Zn, In, Tl, and Hg condensates on a collodion substrate at 20 and 4.2°K indicate a primary crystallite size of ~ 30–100 Å.[279,280] When the films are annealed at a higher temperature their grain size increases and their electrical resistance decreases irreversibly.

During evaporation from the metal, single atoms are emitted together with polyatomic complexes, which become overgrown with atoms in the region of high vapour density close to the evaporator.

The structure and properties of the films are also determined by the angle of incidence of the molecular beam[281]. This effect is most probably due to the fact that the atomic complexes present in the vapour retain some directional motion along the surface when the incidence of the beam is not normal, whereas the single atoms are quickly scattered by the microscopic roughness of the surface. Furthermore, the larger aggregates are more readily oriented in the plane of the surface and are less easily influenced by the microscopic profile. This is consistent with the fact that oriented films on amorphous substrates are obtained much more easily by evaporating the metal in an inert gas

atmosphere than in a vacuum[282]. Thus, fully oriented Ni films with a {110} plane parallel to the substrate are formed on glass in the presence of a 1 mmHg background pressure of argon. These films had a BET surface area and a catalytic activity greater than those of films prepared in a high vacuum by a factor of 2 and 3–5 respectively[283]. Evidently, the vacuum condensates had been formed on smaller aggregates than the deposits obtained in an argon atmosphere.

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Several interesting papers on the preparation and properties of metal aerosol particles have appeared while the manuscript was in press.

Wada[284] has developed a method of volatilisation in a mixed hydrogen–helium plasma, aimed at improving the efficiency of the aerosol method. He obtained 100 Å particles of an Fe–Co–Ni alloy at a gas pressure of 250 mmHg.

Chopra and coworkers[285] prepared very thin films of W, Ta, Mo, Re, Hf, and Zr by evaporating the metal in an argon plasma; there can be no doubt that these films consist of very small aerosol particles. Very interesting structural modifications of the particles are observed at substrate temperatures of 200–400°. Wada has shown[286] that evaporation of many metals in a xenon atmosphere gives particles 3–4 times larger than the particles obtained under the same pressure of argon.

The critical temperature of the transition to the superconducting state has been shown to be abnormally high in granular films consisting of aluminium aerosol particles[287].

Nishida[288] made a detailed study of the shape and structure of manganese particles obtained by evaporating the metal in argon or xenon at low pressures. He observed particles of the high-temperature β-Mn modification as well as α-Mn.

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Institute of Chemical Physics of the
USSR Academy of Sciences, Moscow

U. D. C. 543.544

Thin-layer Chromatography of Biopolymers and Their Derivatives

S.A.Kibardin and V.B.Lazurkina

The modern state of thin-layer chromatography in its application to proteins, nucleic acids, and their derivatives is discussed. Thin-layer chromatography is a new technique in chromatographic analysis which has vigorously developed in recent years. In the review the inadequate development of the thin-layer chromatography of proteins compared, for example, with that of low-molecular-weight compounds is noted and the causes of this situation are analysed. Thin-layer chromatography is compared with other chromatographic methods and the studies on the thin-layer chromatography of biopolymers and their derivatives published up to the present time are critically assessed. New techniques in the thin-layer chromatography of proteins published recently are described.
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I. INTRODUCTION

At the present time chromatographic methods are used on an extremely large scale in a wide variety of branches of science and engineering. These methods have acquired particular importance in biochemistry, molecular biology, and related disciplines. In recent years a new technique—chromatography in thin layers—has been developing rapidly.

Thin-layer chromatography has proved an extremely effective means for the separation and analysis of mixtures of a wide variety of compounds. This method is of interest for chemists, biologists, and medical practitioners working with complex mixtures of natural substances.

The method arose initially as a procedure for the separation of extracts from medicinal plants[1], developing considerably in the period that followed. At the present time several hundred papers in this field are published every year. However, it should be noted that thin-layer chromatography is still used mainly for the analysis of various low-molecular-weight compounds. Studies on the use of thin-layer chromatography for the separation of high-molecular-weight compounds of biological origin, such as proteins and their derivatives, have begun to be published only in recent years, starting with 1962.[2,3]

The application of the thin-layer chromatographic method to proteins and nucleic acids has been developing much more slowly than in the case of low-molecular-weight compounds; thus the total number of studies on the thin-layer chromatography of low-molecular-weight compounds quoted in the bibliography of the Journal of Chromatography for the last two years reaches approximately 1700. On the other hand, the number of studies devoted to the thin-layer chromatography of proteins, nucleic acids, and their derivatives does not exceed 80. This imbalance in the development of the method is particularly notable compared with, for example, the column chromatography of proteins, which has been widely developed and used. Probably the reason for this is partly that until recently thin-layer chromatography as applied to proteins was used mainly as a method for the approximate estimation of the possibility of the separation of protein mixtures, the aim being to achieve the actual separation of the mixture under conditions of column experiments. Thin-layer chromatography then of course plays a subsidiary or auxiliary role. As a method of preparative isolation of proteins, thin-layer chromatography could not compete with the column technique either.

The inadequate theoretical and technical elaboration of the thin-layer chromatography of proteins has also probably retarded the development of this method. However, in recent years it has been shown that the thin-layer chromatography of proteins is by no means merely an auxiliary method and that it can also be of independent value. For example, thin-layer chromatography on different types of Sephadex may be used for the estimation of the molecular weights of the proteins investigated. It is very significant that only 0.1–0.2 mg of the protein is required for such determination[4]. It has also been shown that with the aid of thin-layer chromatography the presence of various groups of proteins can be determined in human blood serum. This requires only 1–2 ml of serum. The method can probably also be of diagnostic value[5,6].

Data indicating the possibility of using thin-layer chromatography for the estimation of various changes due to denaturation of protein molecules caused by external factors is of definite interest too. All these findings show that further development of the thin-layer chromatography of proteins as an independent research technique is promising.

The aim of the present article is to examine the modern state of the thin-layer chromatography of proteins, nucleic acids, and their derivatives, and to indicate new pathways in the development of this field of research, taking into account as far as possible all the experimental studies published in recent years.

II. DEVELOPMENT OF THIN-LAYER CHROMATOGRAPHY AND ITS COMPARISON WITH OTHER CHROMATOGRAPHIC TECHNIQUES

The first studies on thin-layer chromatography were made by the Soviet Scientists Izmailov and Shraiber, who in 1938 used thin layers of alumina to separate the alkaloids of medicinal plants[1]. However, 20 years elapsed before the method received general recognition. In 1958 a new stage in the development of thin-layer chromatography began, mainly in connection with the work of Stahl[7-13]. In these investigations Stahl used thin-layer chromatography for the separation of a wide variety of groups of organic compounds using various adsorbents. The rapid increase of publications on the use of thin-layer chromatography for the separation and identification of various, mainly low-molecular-weight, compounds of biological origin began only after these investigations had been published, approximately in 1960–1961.

Up to the present the thin-layer chromatographic method has been applied to almost all classes of compounds of biological importance. Historically thin-layer chromatography began to develop after techniques such as chromatography of proteins on columns and paper chromatography of amino-acids had been elaborated and received wide recognition.

Compared with column chromatography, thin-layer chromatography has its characteristic features. The entire process is carried out in an open layer and not in a closed column. A significant difference between thin-layer chromatography and column chromatography is also the fact that in the first case the layer of adsorbent is dry (ascending chromatography is most often used). As a result of this, the relative rates of migration of both the eluting buffer and the substance chromatographed are inconstant and R_f varies during chromatography on plates[14].

Compared with thin-layer chromatography, the results obtained in the paper chromatographic method depend very strongly on the properties and structure of the paper sheet itself; furthermore, paper chromatography requires much longer times than thin-layer chromatography. It should also be noted that paper chromatography is nowadays widely used for the separation of low-molecular-weight compounds such as amino-acids but the method has not been developed for the separation of proteins.

Thin-layer chromatography is free of the disadvantages characteristic of paper chromatography. Combining high sensitivity of paper chromatograms and the possibility of using a very small amount of the test substance, thin-layer chromatography has a higher resolving power because of the possibility of using ultrafine adsorbents. Thin-layer chromatography is also characterised by only very slight broadening of the spots of the test compounds and high concentration of the substance in the centre of the spot[15]. The entire chromatographic process requires a very short time and the apparatus and techniques of thin-layer chromatography are distinguished by extreme simplicity and ready availability and can be used in practically any laboratory.

In this respect thin-layer chromatography has advantages over many other methods for the analysis of proteins, which frequently require complex and expensive apparatus. It is interesting that in general advances in chromatography as a whole have been achieved using a very simple technology[16].

In many recently published monographs and reviews dealing with thin-layer chromatography problems concerning technique and partly theoretical problems associated with the application of this new method are discussed quite widely[14,15,17-22], but until recently thin-layer chromatography has been used predominantly for the separation of various low-molecular-weight compounds, mainly of biological origin. The extension of this method to the analysis and investigation of compounds with a high molecular weight, such as proteins, has proved particularly important.

The main principles and technical procedures in thin-layer chromatography are essentially the same for both proteins and compounds of comparatively low molecular weight. The significant difference consists in the fact that other adsorbents and other eluting systems are used in protein chromatography compared with the chromatography of low-molecular-weight compounds. In many reviews and monographs on thin-layer chromatography exhaustive compilations of the adsorbents used in this method as well as the eluting systems and buffer solutions are quoted[14-19,22] and therefore there is no need to consider them in detail. However, it should be noted that all the data quoted in the publications refer almost exclusively to the thin-layer chromatography of low-molecular-weight compounds.

The technical procedures used in the thin-layer chromatography of proteins, nucleic acids, and their derivatives are described below.

III. THE TECHNIQUE OF THE THIN-LAYER CHROMATOGRAPHY OF PROTEINS

1. Adsorbents

In contrast to the thin-layer chromatography of low-molecular-weight compounds, where adsorbents such as silica gel, kieselguhr, alumina, etc. are used, various types of Sephadex (mainly G-75, G-100, G-200, ultrafine varieties), ion-exchange celluloses (DEAE- and TEAE-cellulose, ecteola-cellulose, phosphocellulose) and, among inorganic adsorbents, mainly hydroxyapatite are used for the chromatography of proteins in thin layers.

2. Deposition of the Adsorbent on Plates

Manual method. Different procedures are used: (a) a suspension of the adsorbent is poured on to a plate mounted horizontally; (b) the plate is immersed in the suspension of the adsorbent; (c) the plate is sprayed with a dilute suspension of the adsorbent.

Apparatus of various designs is used in the mechanical method. The apparatus developed by Stahl is most frequently used for the deposition of thin layers[9,22].

3. Procedures Used in the Thin-Layer Chromatography of Proteins

Depending on the direction of movement of the eluting solution, ascending and descending varieties of chromatography are distinguished.

Ascending chromatography. In ascending chromatography the solvent moves up the plate as a result of capillary forces[14]. The chamber for ascending chromatography consists of a vessel with the eluting solution poured on to its bottom in an amount such that a plate with the adsorbent mounted vertically in it is immersed

approximately to a depth of 5 mm. The vessel is tightly closed on top with a lid. The rate of migration of the eluent along the plate is not constant in this case, depending on the path which must be traversed by the solvent, since the capillary forces are balanced by hydrostatic pressure as the liquid rises.

Descending chromatography. In descending chromatography the movement of the eluting solution down the layer of adsorbent is due to hydrostatic forces[15]. Descending chromatography requires a somewhat more complex technique than the ascending procedure. In its simplest version it requires a chromatographic boat (a tube sealed at either end and provided with a slit) into which the eluent is poured and a filter paper bridge is lowered to make contact between the buffer and the upper edge of the plate mounted at a certain angle. Descending chromatography is usually characterised by a constant linear velocity of the eluent. A number of investigators have used descending chromatography on Sephadex[23-25]. Descending countercurrent chromatography, based on a continuous supply of fresh eluting buffer on to the plate (the solution moves to the end of the plate and freely flows away) has been used for proteins[3].

Apart from descending and ascending chromatography there exist also other techniques of thin-layer chromatography: horizontal and circular[14]. These methods have not so far been used for proteins.

4. Eluting Systems for the Thin-Layer Chromatography of Proteins

Phosphate buffer solutions of different concentrations and at different pH are most often used for the thin-layer chromatography of proteins[3,9,23-27]. Depending on whether the concentration of the eluting buffer changes in the chromatographic process, thin-layer chromatography may be regarded as chromatography with constant or variable compositions of the buffer. Usually, for the separation of proteins, the eluting solution is passed once along the plates. However, there also exist methods of repeated chromatography with the same or different eluting buffers. Repeated chromatography in the same eluting system is used to achieve a greater migration of substances with a low R_f value. Before repeating the chromatographic process, the plate is dried.

In stepwise chromatography the eluting buffer is passed repeatedly with increase of its molar concentration.

Gradient chromatography in thin layers. In this case the elution is carried out under the conditions of a concentration gradient, i.e. the concentration of the eluting buffer is altered, usually increased, during chromatography on plates.

Determann[28] developed an apparatus for this type of gradient elution suitable for thin-layer chromatography. The apparatus consists of a glass cylinder mounted on a magnetic stirrer. At a height of 1 cm it is divided by a porous plate into two parts. In the lower part a magnetic stirrer is placed. The capillary tube for the supply of buffer is sealed into the wall of the cylinder. At a distance of 1 cm above the porous plate a tube is sealed into the cylinder for the outflow of the excess liquid. The plate with the adsorbent and the sample deposited on it are put on the porous plate and immersed in the buffer to a depth of 1 cm.

5. Detection of Protein Spots on Plates After Chromatography

Whereas in the thin-layer chromatography of low-molecular-weight compounds, the spots can be identified by a wide variety of reactions, depending on the type of compounds, in experiments with proteins and amino-acids the spots on the plates are usually detected by spraying with ninhydrin[2,26]. Sometimes the plates are covered with filter paper to obtain prints of the protein spots and the paper is then dyed[3,23,29]. The use of fluorescent labels for the detection of proteins in thin layers has also been suggested. For this purpose, the test protein is first treated with a fluorochrome and the distribution of the spots after chromatography is followed using their fluorescence in ultraviolet light[23].

Fluorescent supports with a layer of adsorbent deposited on them can also be employed[30]. Sometimes the fluorescent dyes are first mixed with the adsorbent before its deposition on the plates[14]. The chromatogram can also be sprayed after separation of the mixture of test substances with solutions of fluorescent dyes[22]. In all these cases the test compounds are detected as dark spots against a fluorescent background.

An interesting method for the identification of the test substances was proposed by Heyns and Grutzmacher[31]. They employed a combination of thin-layer chromatography and mass spectrometry for the determination of the derivatives of amino-acids and certain other low-molecular-weight compounds. After being scraped off from the chromatograms, the contents of the spots were introduced directly into a mass-spectrometer for the measurements.

Quantitative methods in thin-layer chromatography usually involve the elution of the substance on the plate followed by the determination of its concentration; or they are based on the determination of the size and colour intensities of the spots formed by the test compound on the plate with the adsorbent[14,15,22]. For example, a quantitative determination of the protein fractions of blood serum after chromatography on Sephadex plates (ultrafine G-100 and G-200) has been demonstrated by Japanese workers[6]. However, it should be noted that quantitative methods in thin-layer chromatography have been used on an inadequate scale compared with, for example, the determination of low-molecular-weight compounds.

IV. THIN-LAYER CHROMATOGRAPHY OF PROTEINS, AMINO-ACIDS, AND THEIR DERIVATIVES

1. Thin-Layer Chromatography of Amino-Acids and Their Derivatives

Mainly silica gel is used as an adsorbent in the thin-layer chromatography of amino-acids; ion-exchange celluloses or cellulose powders have been used to a lesser extent.

In one of the first studies of this kind a mixture of 24 amino-acids was successfully separated on silica gel plates using several solvents[32]. The best results are obtained with the n-butyl alcohol–acetic acid–water mixture and also mixtures of phenol and water. Very good results were achieved when amino-acids were separated on silica gel by two-dimensional chromatography using the chloroform–methanol–ammonia system in one direction and the phenol–water system in another[33]. By this procedure, it proved possible to separate 14 different amino-acids, while paper chromatography under the same conditions revealed

only ten amino-acids. The separation of amino-acids on silica gel with the aid of two-dimensional chromatography has also been achieved in other investigations[34,35]. These workers successfully separated 15 amino-acids on thin cellulose layers in the solvent systems n-butyl alcohol–acetic acid–water, methyl alcohol–water–pyridine, and certain others[36]. Amino-acids have also been satisfactorily separated on thin layers of ion-exchange DEAE-cellulose[37] and also by two-dimensional chromatography on cellulose[38]. Thus the thin-layer chromatography of amino-acids, particularly when the two-dimensional technique was used, proved to be much more effective (approximately by a factor of ten)[30] than the separation of amino-acids by paper chromatography.

Apparently the method of "finger prints" can be successfully used in thin-layer chromatography. Enzymic hydrolysates of human gamma-globulin, horse heart cytochrome, and certain other proteins were treated[39] with dimethylaminonapthalenesulphonyl chloride (fluorochrome). After the removal of the excess of the reagent, the hydrolysis products were separated by two-dimensional chromatography on thin layers of silica gel. It was shown that the results thus obtained agree with those from other methods. The amount of protein required for analysis is then smaller by a factor of ten (about 20 μg). Peptide maps have also been investigated with the aid of thin-layer chromatography[40,41].

The application of thin-layer chromatography to the separation and identification of dinitrophenyl and phenylthiohydantoin derivatives of amino-acids proved to be very promising. Silica gel is most frequently used in such cases. Thus it has been shown that almost all dinitrophenyl derivatives of amino-acids can be successfully separated in a thin layer of silica gel with the aid of both ascending and two-dimensional chromatography in various solvent systems[42–44].

Thin-layer chromatography of dinitrophenyl derivatives of amino-acids has also been used by other investigators[45,46] and Figge[47] and Burgi[48]. These workers used thin-layer chromatography to study urine and other physiological liquids. The thin-layer chromatography of ^{14}C-labelled dinitrophenyl-amino-acids on thin layers of silica gel has been used to study processes occurring in the pyruvic acid cycle[49].

A combination of thin-layer chromatography and quantitative ultramicro analysis of amino-acids in the form [^{14}C]-methyl esters and their dinitrophenyl derivatives were successfully employed in a recent study[50].

Deyl and Rosmus[51] described an interesting application of thin-layer chromatography in which they identified *N*-terminal amino-acids using their sulphonaphthyl derivatives. Fluorescent amino-acid spots can be determined at concentrations of 10^{-10} M. Recently *N*-terminal amino-acids have been determined as their dinitrophenyl derivatives on thin layers of silica gel[52].

Thin-layer chromatography has also been employed for the separation of phenylthiohydantoin derivatives of amino-acids. Thus a mixture of phenylthiohydantoin derivatives of 19 amino-acids has been successfully separated[42] by two- and one-dimensional chromatography on silica gel layers using various solvent systems. In another study[53] a combination of thin-layer chromatography and electrophoresis was employed to separate mixtures of phenylthiohydantoin derivatives of amino-acids, also on silica gel layers.

In a recently published study the thin-layer chromatography of phenylthiohydantoin derivatives of amino-acids was successfully achieved on silica gel[54].

In a number of investigations[55–57] the thin-layer chromatography of phenylthiohydantoin derivatives of amino-acids was used for the analysis of peptides. It should be noted that thin-layer chromatography of dinitrophenyl and thiohydantoin derivatives of amino-acids has certain advantages over paper chromatography. Firstly, in experiments in thin layers there is a considerable economy of time expended on the chromatographic process. Secondly, thin-layer chromatography exhibits high sensitivity, approximately ten times higher than that of paper chromatography. Recently data have been published[58] showing that the use of the optimum silica gel grain size (in the range 2–5 μm) and restriction of the path traversed by the solvent to 4–5 cm permits a sharp improvement (by a factor of 5–10 compared with the usual technique) of the sensitivity of the thin-layer chromatography of dinitrophenyl and phenylthiohydantoin derivatives of amino-acids and also a reduction of the duration of analysis.

This finding unquestionably demonstrates the promise of the thin-layer chromatographic technique for the identification and analysis of amino-acids and their derivatives and also for the separation of protein hydrolysis products and the investigation of complex mixtures of peptides and polypeptides.

2. Thin-Layer Chromatography of Proteins

Three groups of adsorbents are at present used for the thin-layer chromatography of proteins. These are different brands of Sephadex, ion-exchange celluloses, and also hydroxyapatites. Thin-layer chromatography on different types of Sephadex has been most widely used.

The first publications on the thin-layer chromatography of proteins appeared in 1962. These were the studies of Johansson and Rymo[3], who used thin layers of Sephadex, and of Hofmann[2,59], who used hydroxyapatite. Johansson and Rymo were two of the first investigators who used different types of Sephadex for the separation of a number of proteins in thin layers[3,23]. These workers employed G-50, G-75, G-100, and G-200 Sephadex for thin-layer gel filtration. For proteins with relatively low–molecular–weights, the adsorbents used were G-50 and G-75 Sephadex, while for proteins with molecular weights of 100 000 and above the less strongly cross-linked G-100 Sephadex and G-200 Sephadex were employed. The mobility of ceruloplasmin from human serum mixed with various peptides and amino-acids was estimated on G-25 Sephadex. In layers of G-25 Sephadex this protein can be readily separated from amino-acids the mobility of which is much lower. On G-75 Sephadex plates, it proved possible to separate mixtures of oxserum albumin and β- and α-lactoglobulines with molecular weights of 69 000, 35 000, and 15 000 respectively.

A satisfactory separation of tryptic hydrolysate of gamma-globulin from human serum has been achieved on G-75 Sephadex plates. The relevant papers give a detailed description of the conditions used in the preparation of the Sephadex plates.

The use of different types of thin-layers of Sephadex for the estimation of the molecular weights of various proteins is also of interest. It has been shown[4,28] that the molecular weights of the test proteins can be estimated approximately using G-75 and G-200 Sephadex. The following proteins have been employed for this purpose: lysozyme, haemoglobin, gamma-globulin, etc. This application has been developed further by Determann[27], who showed that the volume of the eluting buffer solution is linearly related

to the logarithm of the molecular weight of the test protein. The molecular weights of ribonuclease, chymotryptsin, trypsin, cytochrome *c*, and certain other proteins have also been estimated. Ultrafine G-200 Sephadex was used as adsorbent.

Various types of Sephadex have been used for the thin-layer gel filtration of proteins and mucopolysaccharides by Roberts[60], who described a technique for the preparation of the plates and the procedures employed to identify proteins on Sephadex plates.

Thus the thin-layer chromatography of proteins on different types of Sephadex can probably be used successfully as a simple method for the comparative estimation of the molecular weights of the test proteins. Although the method yields only approximate molecular weights, nevertheless in many cases it is preferable (large saving of time) to determinations by other procedures, requiring a complex apparatus.

A number of studies dealing with the separation of blood serum proteins by thin-layer chromatography have been published recently. Thus in the separation of human blood serum proteins on layers of G-75 Sephadex only one extended protein zone was observed, while on G-100 Sephadex the serum proteins are usually divided into three fractions[23]. It is interesting that the column chromatography of serum proteins on Sephadex also yields three fractions[61]. It has been shown[26] that a mixture of albumin and gamma-globulin from human serum can be successfully separated on phosphocellulose plates. The optimum conditions for the separation of these proteins are achieved with a definite water content in the thin layer of adsorbent, i.e. 70–75%. A decrease or increase of the concentration of water in the adsorbent plates greatly impairs the separation. This investigation showed that for optimum results it is necessary to control the moisture content of the adsorbent used in thin-layer chromatography.

An interesting application of the thin-layer gel filtration of blood serum proteins on Sephadex (ultrafine G-200) was found by Bergström[5], who employed gel filtration for the analysis of pathological human serum proteins under clinical conditions. He discovered that proteins from normal human serum yielded three zones when separated on plates corresponding to the sedimentation constants 4.5 S, 7.0 S, and 19.0 S. The contents of these three groups of proteins in normal serum were respectively 69.7, 24.6, and 5.7%, while pathological serum proteins yielded on gel filtration different percentages, depending on the illness. Analogous results were also obtained by Migita[6] in the thin-layer gel filtration of human blood serum proteins on different types of Sephadex. He employed Sephadex plates (G-100 and ultrafine G-200) on which proteins of normal serum were separated into three zones corresponding to the sedimentation constants 4.0 S, 7.0 S, and 19.0 S. The data on the gel filtration of the proteins from five pathological human blood sera are also quoted.

Italian workers[62] suggested that the thin-layer chromatography on G-200 Sephadex be used to investigate the serum from patients ill with paraproteinemia.

The above data show that thin-layer gel filtration on different types of Sephadex can yield over a comparatively short time (5–6 h) information about the changes in the protein composition of the blood, which should be of undoubted interest for clinicians.

The thin-layer chromatography of certain individual blood serum proteins (haemoglobin, albumin, etc.) has been carried out to estimate their mobility on Sephadex plates (G-100 and G-200)[24,25]. In a recent investigation[63] the authors were able to separate the proteins from normal human blood serum into ten fractions by the combination of thin-layer gel filtration (ultrafine G-200 Sephadex) and electrophoresis, while normal paper electrophoresis shows only five protein components.

The successful separation of haemoglobin and myoglobin on ultrafine Sephadex layers has been recently demonstrated[64,65].

Proteins with enzymic activity have also been subjected to thin-layer chromatography. Willand and Determann[66] used DEAE-Sephadex as an adsorbent for the separation of lactate dehydrogenases.

In other studies[23,29] ribonuclease, lysozyme, chymotrypsin, trypsin, pepsin, alkaline liver phosphatase, and certain other enzymic proteins were chromatographed on different types of Sephadex. In a recent investigation purified preparations of individual proteins were used for preparative estimates of their behaviour on Sephadex plates. It was shown that appropriate types of Sephadex can serve as suitable materials for the preparation of various enzyme proteins.

The use of hydroxyapatite as an adsorbent for the thin-layer chromatography of enzymes has been demonstrated by Kibardin and Lazurkina[67,68], who employed trypsin obtained from various sources, ribonuclease, and certain other enzymes. It was shown that thin layers of hydroxyapatite can be successfully used to estimate the possibility of the separation of protein mixtures and also to characterise the homogeneity and mobility of various enzyme proteins.

Recently thin-layer chromatography on ecteola-MN-300 was used[69] to separate certain coenzymes. The R_f values for eleven coenzymes are quoted. It was shown that some of them are grouped in a single spot. The compositions of the eluting mixtures most suitable for the clear separation of the individual coenzymes are given.

V. THIN-LAYER CHROMATOGRAPHY OF NUCLEIC ACIDS AND THEIR DERIVATIVES

Only comparatively recently thin-layer chromatography began to be applied for the separation of nucleic bases, nucleotides, and nucleosides. Different types of cellulose and to a certain extent silica gels have been mainly used as adsorbents. Other adsorbents have been employed for this purpose much more rarely[70–74].

Randerath[70,71] was the first to use thin-layer chromatography for the analysis of nucleic bases, nucleotides, and nucleosides. The thin-layer chromatography of these compounds has advantages compared with paper chromatography. The boundaries of the spots on the thin layers of adsorbents are much less diffuse than in paper chromatography[73]. Another advantage of thin-layer chromatography is the shorter time required for the separation of the test compounds than in paper chromatography.

The high sensitivity of the thin-layer chromatographic method has also been noted[75]. Ecteola-cellulose has been most frequently used for the separation and analysis of nucleotides and nucleosides. Using this adsorbent, it has proved possible to separate successfully 16 nucleotides in short periods ranging from 4 to 60 min[76]. Ecteola-cellulose has also been used by other investigators[70,71,77,78]. Recently ecteola-cellulose was employed for the thin-layer chromatography of DNA.[79]

A number of studies have dealt with the thin-layer chromatography of nucleic acid derivatives on DEAE-cellulose[77–81]. In one of these[81] a method was proposed

for two-dimensional thin-layer chromatography whereby it is possible to separate a mixture of mono-, di-, and triphosphates of adenosine, cytidine, guanosine, and uridine.

Thin layers of PEI-cellulose have been used for the ascending chromatography of deoxyribo-oligonucleotides [82,83]. Layers of MN-300-cellulose have been employed for the separation of nucleic bases and nucleosides [72,73,82].

DEAE-Sephadex A-25 has also been used as adsorbent in the separation of nucleotides by thin-layer chromatography.

The number of studies published on the application of silica gels for the thin-layer chromatography of nucleic bases and nucleic acid derivatives is much smaller [71,85].

Among inorganic adsorbents, alumina has also been employed for the thin-layer chromatography of nucleic acid derivatives [86]. Thus a comparatively small number of adsorbents have been used for the separation and analysis of nucleic acids and their derivatives by thin-layer chromatography.

Mangold [75] notes that the chromatography of nucleotides and nucleic acids in thin layers of ion-exchange celluloses is superior to all analytical methods for separation employed hitherto. In particular, the considerable saving in time when this method is employed must be pointed out. The high capacity of ion-exchange adsorbents makes it possible to use micro-amounts of the test substance. It is noteworthy that until now thin-layer chromatography has been used largely for the separation of purine and pyrimidine bases of nucleotides and mononucleotides. So far the method has not been applied to the analysis of the hydrolysis products of nucleic acids.

In a comparative assessment of various adsorbents employed in thin-layer chromatography published data show that nucleic bases are better separated from the corresponding nucleotides on layers of eteola-cellulose and other celluloses than on silica gel. On the other hand, the inorganic adsorbent gives better results in the separation of the bases themselves.

The efficiency of the adsorbents is approximately the same in the separation of nucleosides [75]. However, it should be noted that, despite its positive aspects, the thin-layer chromatography of nucleotides and other nucleic acid derivatives is at present essentially in its initial stage of development and has been only weakly developed so far compared with, for example, the column chromatography of nucleic acid. Up to the present time, there have been virtually no studies of the thin-layer chromatography of nucleic acids themselves and their hydrolysis products. Nor have there been any studies on the separation of the carbohydrate components of nucleic acids by thin-layer chromatography although this method might well prove to be quite suitable for the analysis of such compounds.

VI. NEW TECHNIQUES IN THE THIN-LAYER CHROMATOGRAPHY OF PROTEINS

In recent years certain new possibilities of the thin-layer chromatography of proteins and their derivatives have been demonstrated. Thus it has been shown [87] that enzymic reactions can be followed directly on plates. PEI-Celluloses served as the adsorbent.

As already mentioned, thin-layer chromatography has been successfully employed also for the analysis of the "peptide maps" of protein hydrolysates. Thus the possibility of the separation of the hydrolysis products of proteins by thin-layer chromatography on silica has been demonstrated [88] for myosine and protamine as examples.

Usually the complex mixture of hydrolysis products is separated by paper chromatography. A definite advantage of thin-layer chromatography over paper chromatography consists in much greater sensitivity [41] (approximately by a factor of ten).

The combination of thin-layer chromatography with electrophoresis in thin layers has proved very promising [63,89-91]. It has been shown in one of these investigations [89] that blood serum proteins can be separated into twelve components with the aid of chromatography and electrophoresis on G-100 and ultrafine G-200 Sephadex plates.

By combining electrophoresis and chromatography, Glaesner et al. [91] succeeded in separating the mixture of the hydrolysis products of haemoglobin into 28 peptides on silica gel plates.

In studies combining thin-layer electrophoresis and chromatography different types of Sephadex have been used as adsorbents for proteins and silica gel has been used for the separation of peptides.

The number of such studies is so far small. Nevertheless further developments of this technique are likely to be very promising. Bearing in mind the technical simplicity of thin-layer chromatography, this method can probably be successfully used also in clinical laboratories [62,92]. The investigations in this field are still very few.

Studies in which a combination of thin-layer chromatography and immunodiffusion are combined merit attention [93,94]. They demonstrated the possibility of thin-layer immunochromatography using as example serologically active proteins. The adsorbents were different types of DEAE-Sephadex. However, it should be noted that thin-layer immunochromatography has not so far been developed any further. The scope of this method appears at the present time to be more limited than that of Grabar's immunoelectrophoresis [75].

An interesting application of thin-layer chromatography under the conditions of the so called "barrier" method has been demonstrated [96]. Here the separation of oligonucleotides as a function of chain length and composition and chromatographic temperature can be achieved on cellulose plates. The same investigation demonstrated the possibility of detecting by thin-layer chromatography specific molecular complexes formed between poly- and oligonucleotides.

The possibility of estimating by thin-layer chromatography various changes due to modification and denaturation in proteins occurring under the action of external agents has been demonstrated recently. Immune human gamma-globulins treated with urea solutions at different concentrations show a reduced mobility in chromatography on hydroxyapatite plates. The decrease of the mobility of the proteins on plates takes place in parallel with the degree of the denaturing effect of urea on the gamma-globulin molecule. The biological activity of these proteins changed correspondingly. It is also interesting that the renaturation of immune globulins is likewise accompanied by the recovery of their mobility on adsorbent plates up to the normal level [97].

In another investigation it was shown that the treatment of human serum gamma-globulin with heavy metal salt solutions leads to a change in the mobility of this protein in chromatography on thin layers of hydroxyapatite compared with control experiments [68].

The above studies show that thin-layer chromatography can probably also serve for the assessment of the changes in proteins which are reflected in their surface and adsorption properties.

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The data presented above show quite convincingly the wide use of thin-layer chromatography in protein chemistry. In conclusion we must briefly consider the principal factors determining the further development of the thin-layer chromatography of proteins.

At present we are in the initial stage of the development of this method as applied to proteins and nucleic acids. Its advantages—rapidity, high sensitivity, and the possibility of its application in mass analyses—are unquestionable. All these factors make the development of the thin-layer chromatography of proteins very promising. The problems next to be resolved in this field involve the necessity of further theoretical and practical development of the method, the elaboration of the technique, the selection of new adsorbents, and the widening of the range of proteins investigated. The development of new techniques in the thin-layer chromatography of proteins, particularly those involving the combination of different methods, are also extremely important: for example, thin-layer electrophoresis–chromatography, thin-layer immunochromatography, etc. The thin-layer chromatography of fluorescent protein complexes and new technical methods should be more widely used. These new developments will ensure the final promotion of thin-layer chromatography from a subsidiary method to one of independent importance in the study of biopolymers.

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Pasteur Institute of Epidemiology and Microbiology, Leningrad